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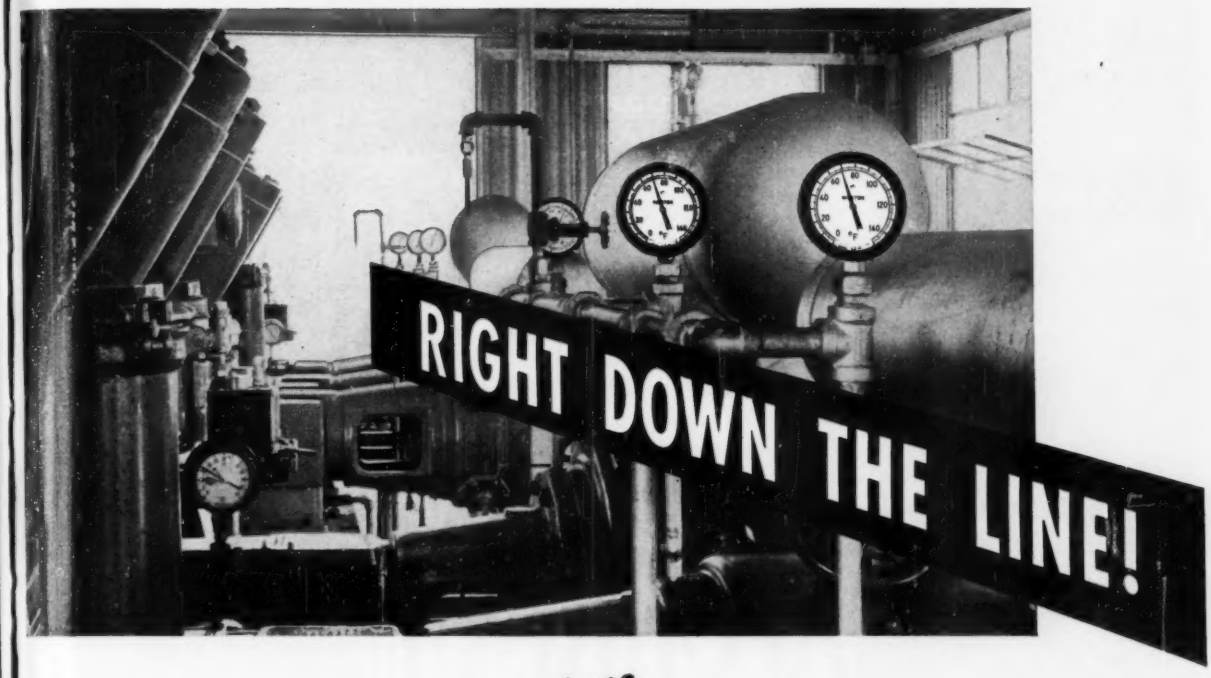

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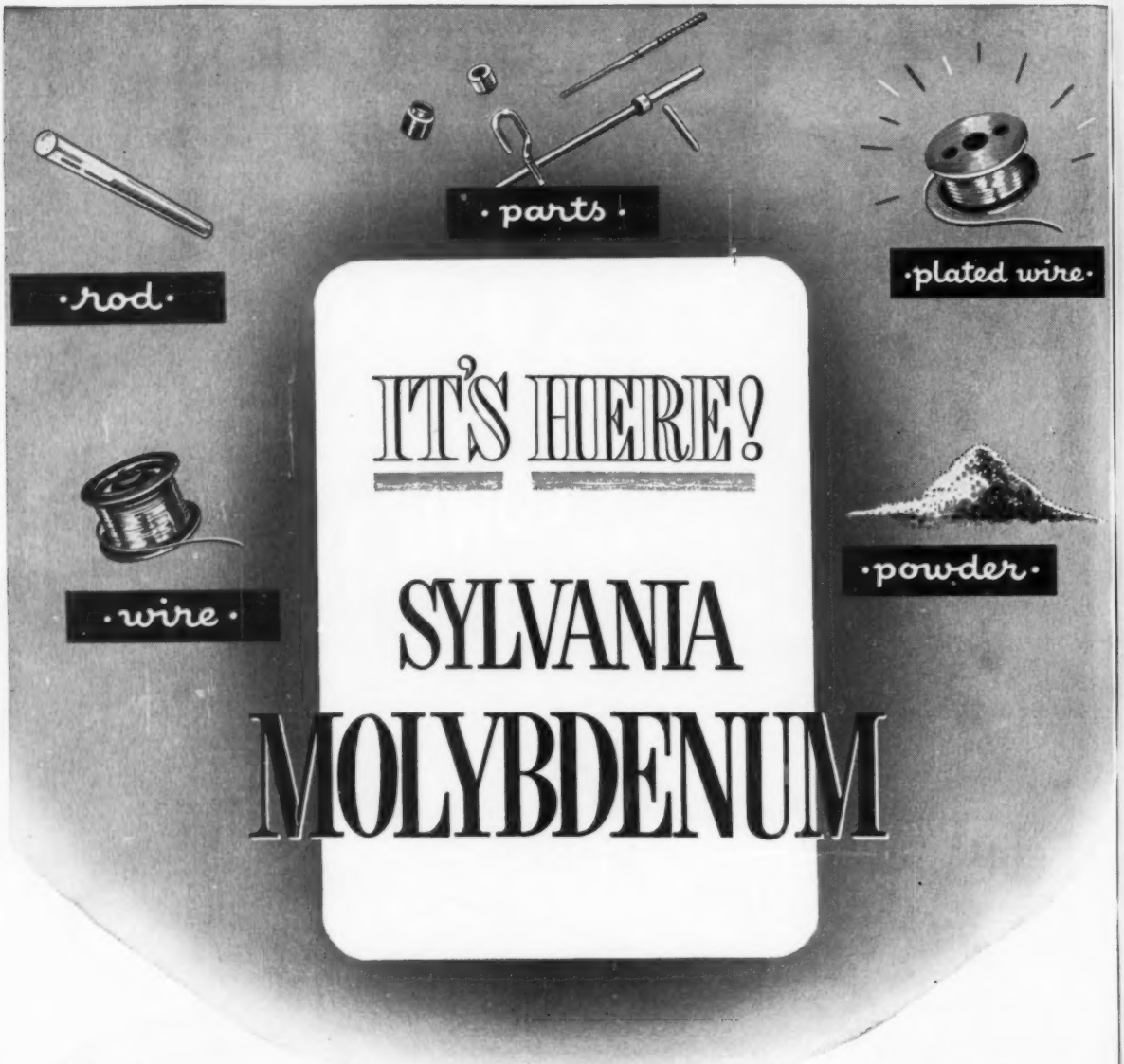

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Editorial

Plans for Corrosion Research

THE CRITICAL NEED of fundamental knowledge of metallic corrosion has led the Engineering Foundation to sponsor the organization of a Corrosion Research Council and to undertake the accumulation of funds for the support of a comprehensive long-range research program. The leading companies in American industry will be invited to contribute up to approximately one hundredth of one per cent of their annual profits toward this fund. It will be pointed out that this will represent only a small fraction of what corrosion is costing them and an even smaller fraction of what these companies can expect to gain from a better knowledge of how to control corrosion.

The scale of the proposed effort is indicated by the initial goal of $200,000, to be spent eventually at a rate of $100,000 a year. The Corrosion Council will be composed of representatives from sponsoring industry groups, technical societies, and government organizations. The Council will have the primary responsibility for activating basic scientific studies in corrosion. It will originate and will receive proposals for fundamental research and will select qualified scientific groups to carry them out. Advisory subcommittees of the Council will act as liaison between the Council and directors of the research programs and will undertake to see that the objectives of the Council and the sponsors are being achieved.

The Electrochemical Society will welcome the creation of the Corrosion Research Council and will endorse the plans for a continuing program of long-range scientific research in the field of corrosion. The present technology of corrosion control is based upon rather meager scientific data, and it is very likely that the concerted effort of scientists in the underlying disciplines of electrochemistry, physical metallurgy, solid state physics, and surface chemistry will in time provide the new knowledge that is so essential to further substantial progress in the reduction of the gigantic cost of corrosion to modern industrial society. It will be recalled that Professor H. H. Uhlig, after a careful study, has estimated the annual loss due to corrosion in the United States alone to be over five billion dollars. It will require only modest success in the new program to achieve huge savings both in dollars and in natural resources!

The Educational Situation

President Eisenhower's proposal of federal encouragement of a large program of school building construction focuses attention on a problem that has long been acute and will become intolerable within the next decade unless remedial action is taken now. The President wisely places emphasis upon the importance of proceeding at the community level and avoiding political domination. Direct financial support of the public school system is undesirable, but it is clear that the problem has become too great in magnitude for many communities to cope with without guidance and some form of assistance. The deficiency of classrooms and physical facilities is but a part of the scandalous educational situation facing the country today. Shockingly low teacher salaries, inadequately trained and poorly qualified teachers, and no teachers at all for many schools and many subjects—particularly the sciences—present a problem that is second in importance only to that of national defense! —RMB

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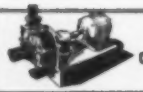
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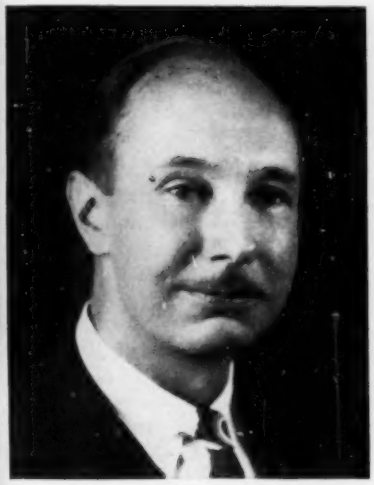

HERBERT H. UHLIG

SHERLOCK SWANN, JR.

LYLE I. GILBERTSON

As a result of the recent annual election, in which the voting is by mail ballot, Herbert H. Uhlig has been elected the new President of the Society, Sherlock Swann, Jr., Third Vice-President, and Lyle I. Gilbertson is Treasurer. The new officers will be presented to the members and will formally take office at the annual business meeting of the Society, which will take place following the Society Luncheon on Tuesday, May 3, at the Cincinnati Meeting.

Dr. Uhlig, Professor of Metallurgy in charge of the Corrosion Laboratory at Massachusetts Institute of Technology, Cambridge, Mass., replaces Mr. Marvin J. Udy, consultant in metallurgical and electrochemical engineering, Niagara Falls, N. Y. Mr. Udy, as Past President, will continue as a member of the Board of Directors.

Sherlock Swann, Jr., Research Professor of Chemical Engineering at the University of Illinois, Urbana, Ill., will start his first term as Society Vice-President and will serve with the two previously elected Vice-Presidents, Hans Thurnauer and Norman Hackerman.

Lyle I. Gilbertson, Director of the Murray Hill Laboratories of Air Reduction Company, Inc., Murray Hill, N. J., begins his three-year term as Treasurer, replacing E. Gideon Widell, RCA Victor Division, Harrison, N. J. Mr. Widell has been active in Society affairs since 1930, serving as Treasurer from 1949 to the present.

See Your Program Booklet

Complete details of the Cincinnati Meeting schedule will be found in the Program Booklet which has been mailed to all Society members. Dates of the meeting are May 1–5, with headquarters at the Sheraton-Gibson Hotel.

Guest Speaker

Dr. Gustav Eckstein, University of Cincinnati, will address the Society Luncheon on Tuesday, May 3. His talk is entitled "At Arms Length."

Cincinnati Technical Program

Monday, May 2, 1955

9:00 A.M.—Formal Opening of the 107th Convention, with Introduction by General Chairman Roy O. McDuffie and response by President Marvin J. Udy.

Electric Insulation

Monday, May 2, 1955

Radiation and Dielectrics with R. A. Ruscetta presiding

9:30 A.M.—Welcome—C. F. Miller.

9:45 A.M.—"The Measurement of Radiation Affecting Insulation" by W. W. Managan, Victoreen Instrument Co., Cleveland, Ohio.

10:15 A.M.—"Electron Irradiated Polyethylene" by J. R. Stirrat and P. A. Goodwin, General Electric Co., Pittsfield, Mass.

10:45 A.M.—"Radioactive Isotopes in the Study of Dielectric Degradation" by H. C. Beachell and V. L. Turner, University of Delaware, Newark Del.

11:15 A.M.—"Synthesis of Electrical Insulation by Means of Gamma

Radiation" by T. D. Callinan, Naval Research Lab., Washington, D. C.

Electric Insulation

Monday, May 2, 1955

Electrical and Mechanical Properties of Plastics
with A. J. Sherburne presiding

2:00 P.M.—"Properties of Gafite" by H. D. Anspon, Central Research Labs., General Aniline and Film Corp., Easton, Pa.

2:30 P.M.—"Casting Resins for the Electrical Trade" by W. E. Harvey, John C. Dolph Co., Monmouth Junction, N. J.

3:00 P.M.—"Properties of Polyamide-Epoxy Resin Casting Compositions" by Wm. Minarik, General Mills Inc., Minneapolis, Minn.

Round Table

with L. L. Deer presiding

3:30 P.M.—Round-table Discussion of Casting Resins, with a panel of experts.

Electric Insulation

Tuesday, May 3, 1955

Solid Insulation
with M. D. Heyman presiding

9:00 A.M.—"Semiceramics" by M. D. Heyman, Integrated Mica Corp., Woodmere, N. Y.

9:30 A.M.—"Inorganic and Organic Synthetic Fiber Papers for Reinforced Plastic Laminates" by A. F. Arledter, Hurlbut Paper Co., South Lee, Mass.

10:00 A.M.—"The Manufacture and Properties of a Novel Reinforced Plastic" by J. W. Case, Bureau of Ordnance, Navy Department, Washington, D. C., and J. D. Robinson, Firestone Tire and Rubber Co., Akron, Ohio.

10:30 A.M.—"Epoxy Resin Glass Base Laminates" by J. C. Pitzer, Formica Co., Cincinnati, Ohio.

11:00 A.M.—"The Electrical Resistivity of Bonded Micaceous Materials at Elevated Temperatures" by Kenneth Wechsler, Mica Insulator Co., Schenectady, N. Y.

Electric Insulation

Tuesday, May 3, 1955

Electrical Properties of Resins
with J. R. Bukey presiding

2:00 P.M.—"The Properties of Exon" by J. R. Bukey, Firestone Plastics Co., Pottstown, Pa.

2:30 P.M.—"The Electrical Conductivity of Carbon Black Reinforced Elastomers" by Gerard Kraus and J. F. Svetlik, Phillips Petroleum Co., Bartlesville, Okla.

3:00 P.M.—"Heat Stability of the Resole Type Phenol-Formaldehyde Resins" by A. H. Haroldson, Continental-Diamond Fibre Co., Newark, Del.

3:30 P.M.—"The Past, Present, and Future of Prefabricated Wiring (Printed Circuits)" by Carl Coy, Consulting Engineer, Tammen and Denison, Chicago, Ill.

Electric Insulation

Wednesday, May 4, 1955

Electrophysics
with T. D. Callinan presiding

9:00 A.M.—"Organic Peroxides as Source of Cations" by Andrew Gemant, Detroit Edison Co., Detroit, Mich.

9:30 A.M.—"Recent Developments in Power and Allied Products" by N. R. Maleady, General Electric Co., Rome, Ga.

10:00 A.M.—"Recent Developments in Electrical Measurements" by J. A. Connor, Radio Corp. of America, Camden, N. J.

10:30 A.M.—"Dielectric Properties of Aerosols" by H. C. Thacher, Jr., Aeronautical Research Lab., Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

11:00 A.M.—"Effects of Moisture, Temperature, and Frequency on the Electrical Properties of Insulating Materials" by L. J. Frisco, Institute for Cooperative Research, The Johns Hopkins University, Baltimore, Md.

11:20 A.M.—"Breakdown Phenomena as Related to Other Dielectric Properties" by J. J. Chapman, Institute for Cooperative Research, The Johns Hopkins University, Baltimore, Md.

11:45 A.M.—"Inhibiting Effects of 2/6-Di-Tertiary-Butyl Para Cresol on Cellulose Insulation Deterioration" by E. D. Andrews, Koppers Co., Pittsburgh, Pa., and F. C. Doble, Doble Engineering Co., Cambridge, Mass.

Electric Insulation

Wednesday, May 4, 1955

Capacitors
with D. A. Lupfer presiding

2:00 P.M.—"Liquid Filled Capacitors" by Sydney Wald, Glenn L. Martin Co., Baltimore, Md.

2:30 P.M.—"Recent Developments in Electrolytic Capacitors" by Judson West, Jr., Magnavox Co., Fort Wayne, Ind.

3:00 P.M.—"High Voltage Glass Capacitors" by Gail Smith, Corning Glass Works, Corning, N. Y.

3:30 P.M.—"Subminiature Capacitors and Other Components" by Louis Kahn, Aerovox Corp., New Bedford, Mass.

4:00 P.M.—"Capacitors for High Temperature Pulse-Forming Networks" by William Allison, Sprague Electric Co., North Adams, Mass.

Electronics—Luminescence

Tuesday, May 3, 1955

Basic Phenomena
with F. E. Williams presiding

9:10 A.M.—Introduction of Keynote Speaker by Herbert Bandes.

9:15 A.M.—Keynote Address—"The Theoretical Basis for Photoluminescence, Electroluminescence, and Photoelectroluminescence" by F. E. Williams, Research Lab., General Electric Co., Schenectady, N. Y.

10:00 A.M.—"Influence of Electric Fields on Ultraviolet-Excited Phosphors" by Frank Matossi and Sol Nudelman, U. S. Naval Ordnance Lab., White Oak, Md.

10:20 A.M.—"Dielectric Behavior of Electroluminescence" by Willi Lehmann, Westinghouse Electric Corp., Bloomfield, N. J.

10:40 A.M.—"Electroluminescence of Zinc Sulfide Single Crystals" by D. R. Frankl, Physics Labs., Sylvania Electric Products Inc., Bayside, N. Y.

11:00 A.M.—"Effect of Electron Traps on Electroluminescence" by P. D. Johnson, W. W. Piper, and F. E. Williams, Research Lab., General Electric Co., Schenectady, N. Y.

11:15 A.M.—"Infrared Quenching of Cadmium Sulfide Photoconductivity" by S. H. Liebson, U. S. Naval Research Lab., Washington, D. C.

11:35 A.M.—"Recombination Processes in Cadmium Sulfide" by John Lambe, U. S. Naval Research Lab., Washington, D. C.

Electronics—Luminescence

Tuesday, May 3, 1955

with F. E. Williams presiding

2:00 P.M.—"Sensitized Luminescence in NaCl:Ag + Cu" by E. W. Claffy and C. C. Klick, U. S. Naval Research Lab., Washington, D. C.

2:20 P.M.—"Fluorescence of Thallium-Activated Halide Phosphors, I. Spectra of NH_4Br:Tl" by K. H.

Butler, Sylvania Electric Products Inc., Salem, Mass.

2:40 P.M.—"Fluorescence of Thallium-Activated Halide Phosphors, II. Spectra of KCl:Tl" by K. H. Butler, Sylvania Electric Products Inc., Salem, Mass.

3:00 P.M.—"Some General Considerations on the Preparation of Oxygen Dominated Phosphors" by J. L. Ouweltjes and W. L. Wanmaker, Phosphor Div., N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands.

3:20 P.M.—"Activator Systems in Sulfide and Halophosphate Phosphors" by J. S. Prener and F. E. Williams, Research Lab., General Electric Co., Schenectady, N. Y.

3:40 P.M.—"Controlled Preparation and X-Ray Investigation of Cadmium Sulfide" by F. Schossberger, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.

4:00 P.M.—"Retention of Chloride in Fired Zinc Sulfide" by P. Goldberg, D. J. Bracco, and A. Kremheller, Chemistry Lab., Sylvania Electric Products Inc., Flushing, N. Y.

4:20 P.M.—"Particle Size and Structure of Fired Zinc Sulfide Powders" by A. Kremheller, P. Goldberg, and D. J. Bracco, Chemistry Lab., Sylvania Electric Products Inc., Flushing, N. Y.

4:40 P.M.—"The Oxidation of Zinc Sulfide Precipitates to Zinc Sulfate" by D. T. Palumbo and A. K. Levine, Chemistry Lab., Sylvania Electric Products Inc., Flushing, N. Y.

Electronics—Luminescence

Wednesday, May 4, 1955

Specific Phosphor Behavior
with K. H. Butler presiding

9:00 A.M.—"Lead and Manganese-Activated Cadmium Fluorophosphates" by R. W. Wollentin, Research Dept., Westinghouse Electric Corp., Bloomfield, N. J.

9:20 A.M.—"Calcium Halophosphate Phosphors, II. Optical Properties of the Particle Surface" by M. J. Bergin, K. H. Butler, and H. H. Homer, Sylvania Electric Products Inc., Salem, Mass.

9:40 A.M.—"A New Blue-Emitting Phosphor with Manganese Activator" by E. L. Lind, RCA Labs., Radio Corp. of America, Princeton, N. J.

10:00 A.M.—"Magnesium Fluosilicate Phosphors" by P. W. Ranby and S. T. Henderson, Thorn Electrical Industries, Ltd., London, England.

10:20 A.M.—"Preliminary Studies of the Perowskite-Type Ternary Oxides as Luminophors" by Salvador Terol and Roland Ward, Chemical Labs., University of Connecticut, Storrs, Conn.

10:40 A.M.—"Two Arsenate Phosphors and the Significance of Their Emission" by G. R. Fonda, General Electric Co., Cleveland, Ohio.

11:00 A.M.—"The System Cadmium Oxide-Boric Oxide" by E. C. Subbarao and F. A. Hummel, School of Mineral Industries, Dept. of Ceramics, Pennsylvania State University, State College, Pa.

11:20 A.M.—"Luminescent Screens Made by Vapor Reaction" by D. A. Cusano and F. J. Studer, Research Lab., General Electric Co., Schenectady, N. Y.

11:40 A.M.—"Cathodoluminescent Lamps" by L. R. Koller, Research Lab., General Electric Co., Schenectady, N. Y.

12:00 M.—"Color Shifts in Zn-Cd-S (Ag) Phosphors" by Vanja Srepel, General Electric Co., Electronics Park, Syracuse, N. Y.

Electronics—Luminescence

Wednesday, May 4, 1955

Round Table
with Roland Ward presiding

2:00 P.M.—1. Continuation of discussion of papers presented at three previous sessions.

2. "Late News Items," ten minutes each.

3. General discussion.

Electronics—Oxide Cathodes

Monday, May 2, 1955

with J. G. Buck presiding

2:00 P.M.—Introductory remarks by C. P. Hadley.

2:05 P.M.—Keynote Address—"Fundamental Phenomena of Thermionic Emission" by W. B. Nottingham, Massachusetts Institute of Technology, Cambridge, Mass.

2:50 P.M.—"A New Sintered Tungsten Matrix Cathode" by E. A. Thurber, Bell Telephone Labs., Murray Hill, N. J.

3:20 P.M.—"Some Studies on Problems Associated with the Molded Nickel Cathode" by I. J. Bell and G. R. Brewer, Electron Tube Lab., Hughes Research and Development Labs., Culver City, Calif.

3:35 P.M.—"Some Applications of L Cathodes" by J. Babakian, A. Matthewson, and J. Bloom, Air Force Cambridge Research Center, Boston, Mass.

4:00 P.M.—"Manufacturing Advantages of the Philips Impregnated Cathode Used in Magnetron Applications" by Markus Nówogrodzki, Amperex Electronic Corp., Hicksville, N. Y.

4:15 P.M.—"Emission from Molybdenum Activated with Barium" by R. H. Ahlert and E. S. Rittner, Philips Labs., Irvington-on-Hudson, N. Y.

4:35 P.M.—"An Investigation of the Impregnated Cathode" by W. C. Rutledge, E. S. Rittner, and R. H. Ahlert, Philips Labs., Irvington-on-Hudson, N. Y.

Electronics—Oxide Cathodes

Tuesday, May 3, 1955

with L. S. Nergaard presiding

9:30 A.M.—"Improved Philips 'Impregnated Cathode'" by Roberto Levi, Philips Labs., Irvington-on-Hudson, N. Y.

9:45 A.M.—"Chemical Processes in Thin-Film Dispenser Cathodes" by R. C. Hughes and P. P. Coppola, Philips Labs., Irvington-on-Hudson, N. Y.

10:05 A.M.—"A New Pressed Dispenser Cathode" by P. P. Coppola and R. C. Hughes, Philips Labs., Irvington-on-Hudson, N. Y.

10:35 A.M.—"Thermionic Emission Evaluation of Single Constituent Additives in Pure Nickel Cathodes" by F. T. Hill, Raytheon Manufacturing Co., Newton, Mass.

11:05 A.M.—"Application of Automatic Recording Instruments to the Measurement of Emission" by A. N. Yeaton and C. D. Richard, Jr., Superior Tube Co., Norristown, Pa.

11:30 A.M.—"A Simplified Gas Adsorption Method for the Determination of Surface Area of Fine Powders" by D. T. Palumbo, F. M. Starkweather, and D. J. Bracco, Chemistry Lab., Sylvania Electric Products Inc., Flushing, N. Y.

Electronics—Oxide Cathodes

Tuesday, May 3, 1955

with E. A. Coomes presiding

2:00 P.M.—"Electrical Properties of the Oxide Cathode Coating" by Ralph Forman, National Bureau of Standards, Washington, D. C.

2:30 P.M.—"Activation of an Oxide Cathode by Ba, Sr, Ca, and Mg Deposited via a Mass Spectrometer" by R. M. Matheson and R. H. Plum-

lee, RCA Labs., Radio Corp. of America, Princeton, N. J.

3:00 P.M.—"Mass Spectrometric Study of the Field Dependent Evolution of Constituents of a BaO Cathode" by R. H. Plumlee, RCA Labs., Radio Corp. of America, Princeton, N. J.

3:30 P.M.—"Factors Influencing the Particle Size in the Preparation of Alkaline Earth Carbonates" by D. T. Palumbo, D. J. Bracco, and A. K. Levine, Chemistry Lab., Sylvania Electric Products Inc., Flushing, N. Y.

4:00 P.M.—Round-table discussion.

Electronics—Phosphor Application

Thursday, May 5, 1955

with Channing Dichter presiding

9:30 A.M.—Introductory remarks by Channing Dichter.

9:40 A.M.—"Particle Size Methods for TV Phosphors" by J. Rabatin, E. Palik, and R. Gale, Lamp Dept., General Electric Co., Cleveland, Ohio.

10:10 A.M.—"The Use of Polyvinyl Alcohol in the Preparation of Color Phosphor Screens" by The Staff, Parlin Labs., E. I. du Pont de Nemours and Co., Parlin, N. J.

10:45 A.M.—"Kelvin Method of Screen Potential Measurement and Screen Changing" by J. T. Young, Research Lab., General Electric Co., Schenectady, N. Y.

11:15 A.M.—"Ion Focusing Fields and Ion Deterioration Effects on Cathode Ray Tube Screens" by W. A. Thornton, Research Lab., General Electric Co., Schenectady, N. Y.

11:45 A.M.—"Secondary Electron Yields of Screen Materials" by A. B. Laponsky, Research Lab., General Electric Co., Schenectady, N. Y.

12:15 P.M.—Late News Papers.

Electronics—Phosphor Application

Thursday, May 5, 1955

Round Table
with M. Sadowsky presiding

2:00 P.M.—Round-table discussion.

Electronics—Semiconductors

Wednesday, May 4, 1955

Elemental Semiconductors
with N. B. Hannay presiding

9:00 A.M.—Introductory remarks by F. J. Biondi.

9:05 A.M.—"Properties of Germanium and Silicon" by E. M. Conwell, Sylvania Electric Products Inc., Bayside, N. Y.

9:30 A.M.—"Injection and Extraction" by Ralph Bray, Purdue University, Lafayette, Ind.

10:00 A.M.—"The Germanium-Oxygen System" by Donald Tuomi and E. S. Candidus, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

10:30 A.M.—"Donor-Acceptor Balance in Selenium Rectifiers" by H. W. Henkels, Westinghouse Electric Corp., Pittsburgh, Pa.

11:00 A.M.—"Correlation of Electrical Properties of Selenium Rectifiers with Fundamental Bulk Properties" by H. W. Henkels, Westinghouse Electric Corp., Pittsburgh, Pa.

11:30 A.M.—Ten-minute papers of "late news" type. Titles and short abstracts will be available at the Registration Desk.

Electronics—Semiconductors

Wednesday, May 4, 1955

Surface Controlled Phenomena
with J. E. Thomas presiding

2:00 P.M.—"Review of the State of Semiconductor Surfaces" by R. H. Kingston, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

2:30 P.M.—"Ultrahigh Vacuum Studies on Germanium Surfaces" by F. G. Allen, Harvard University, Cambridge, Mass.

3:00 P.M.—"Theory of Surface-Barrier Electrodes" by W. E. Bradley, Philco Corp., Philadelphia, Pa.

3:30 P.M.—"Holes and Electrons in Germanium Electrodes" by C. G. B. Garrett and W. H. Brattain, Bell Telephone Labs., Murray Hill, N. J.

4:00 P.M.—"Effect of Surface Treatments in Low Pressure Gas Atmospheres on Characteristics of Evaporated Surface-Barrier Rectifiers" by P. A. Hartig, Philco Corp., Philadelphia, Pa.

4:30 P.M.—"Effect of Water Vapor on Germanium and Silicon Junctions" by J. T. Law and P. S. Meigs, Bell Telephone Labs., Murray Hill, N. J.

5:00 P.M.—"Observations of Channel Formation on N- and P-Type Semiconductors" by R. N. Noyce, Philco Corp., Philadelphia, Pa.

5:30 P.M.—"Oxidation of Clean Surfaces of Germanium below 25°C" by Mino Green and J. A. Kafalas, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

Electronics—Semiconductors

Thursday, May 5, 1955

Process Technology
with F. J. Biondi presiding

9:00 A.M.—"Etches for Imperfections in Silicon and Germanium" by J. W. Faust, Jr., Westinghouse Electric Corp., East Pittsburgh, Pa.

9:30 A.M.—"Theory of Jet Etching; Electrolytic Etching of Semiconductors" by W. E. Bradley, Philco Corp., Philadelphia, Pa.

10:00 A.M.—"The Purification of Germanium; The Germanium Tetrachloride-Arsenic Trichloride System" by Mino Green and J. A. Kafalas, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

10:30 A.M.—"New Method for Producing High Purity Silicon" by Gustav Szekely, Sylvania Electric Products Inc., Flushing, N. Y.

11:00 A.M.—"Depth of Surface Damage Due to Abrasion on Germanium" by T. M. Buck and F. S. McKim, Bell Telephone Labs., Murray Hill, N. J.

11:30 A.M.—"Electrochemical Preparation of Germane" by Mino Green and P. H. Robinson, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

12:00 M.—Ten-minute papers of "late news" type. Titles and short abstracts will be available at the Registration Desk.

Electronics—Semiconductors

Thursday, May 5, 1955

Semiconducting Alloys and Compounds
with P. H. Keck presiding

2:00 P.M.—"The Present Status of Intermetallic Semiconductors" by R. G. Breckenridge, National Bureau of Standards, Washington, D. C.

2:30 P.M.—"Effect of Zone-Refining Variables on the Segregation of Impurities in InSb" by T. C. Harman, R. K. Willardson, H. L. Goering, and A. C. Beer, Battelle Memorial Institute, Columbus, Ohio.

3:00 P.M.—"Photoeffects in InSb" by S. W. Kurnick, A. E. Goldberg, G. M. Mitchell, and R. N. Zitter, Midway Labs., University of Chicago, Chicago, Ill.

3:30 P.M.—"Effect of Impurities on Photoconductive CdS, CdSe, and PbS" by W. B. Hugle, Baldwin Piano Co., Cincinnati, Ohio.

4:00 P.M.—"Experiments on the Formation of Anode Films on InSb"

by J. F. Dewald, Bell Telephone Labs., Murray Hill, N. J.

4:30 P.M.—Ten-minute papers of a "late news" type. Titles and short abstracts will be available at the Registration Desk.

Electrothermics and Metallurgy

Monday, May 2, 1955

with H. S. Newhall presiding

9:15 A.M.—"Electric Smelting Furnaces" by M. J. Udy, Consulting Engineer, 546 Portage Rd., Niagara Falls, N. Y.

9:45 A.M.—"The Use of Electric Furnaces by the Bureau of Mines in Ferroalloy Research" by N. B. Melcher, Ferrous Metals and Alloys Branch, U. S. Department of the Interior, Bureau of Mines, Washington, D. C.

10:15 A.M.—"High Speed Electrohydraulic Arc Furnace Control" by W. Nordin, Aros Electric, Inc., New York, N. Y.

10:45 A.M.—"The Trend in Electric Furnace Design Particularly As It Applies to the Production of Calcium Carbide" by J. C. Bode, National Carbide Co., New York, N. Y.

Electrothermics and Metallurgy

Monday, May 2, 1955

with H. S. Newhall presiding

2:30 P.M.—"The Ferroalloy Industry in Australia" by R. H. Hooper, Ferroalloy Plant, Broken Hill Pty. Co. Ltd., Newcastle, N.S.W., Australia.

3:00 P.M.—"Materials Preparation for a Ferroalloy Operation" by D. E. Stingel, Alloy Works, Electro Metallurgical Co., Alloy, W. Va.

3:30 P.M.—"Materials Handling and Preparation of Raw Materials for Ferroalloy Furnaces" by R. A. Davidson, Vanadium Corp. of America, Niagara Falls, N. Y.

Electrothermics and Metallurgy

Tuesday, May 3, 1955

Oxidation and Corrosion
with A. A. Burr presiding

2:00 P.M.—"Thermodynamics of the Oxidation of Chromium" by J. N. Ramsey, D. Caplan, and A. A. Burr, Rensselaer Polytechnic Institute, Troy, N. Y.

2:30 P.M.—"High Temperature Oxidation of Two Zirconium-Tin Alloys" by M. W. Mallett and W. M. Albrecht, Battelle Memorial Institute, Columbus, Ohio.

3:00 P.M.—"Reaction of Nitrogen with Uranium" by M. W. Mallett and A. F. Gerds, Battelle Memorial Institute, Columbus, Ohio.

3:30 P.M.—"Oxide Nucleation and the Substructure of Metals" by E. A. Gulbransen, W. R. McMillan, and K. F. Andrew, Research Labs., Westinghouse Electric Corp., East Pittsburgh, Pa.

4:00 P.M.—"Erosion of Steel by Gases" by M. J. Fraser and A. A. Burr, Rensselaer Polytechnic Institute, Troy, N. Y.

4:30 P.M.—"Stress Corrosion Cracking in Magnesium" by D. K. Priest and M. G. Fontana, Ohio State University, Columbus, Ohio.

Electrothermics and Metallurgy

Wednesday, May 4, 1955

Electrochemical Techniques in Metallurgical Research
with J. H. Westbrook presiding

Thermodynamics

9:00 A.M.—"Electrochemical Techniques in Thermodynamics" by R. A. Oriani, Research Lab., General Electric Co., Schenectady, N. Y.

Mechanical Properties

9:30 A.M.—"Relations between Mechanical Deformation and Thermoelectric Force" by J. M. Berry, Research Lab., General Electric Co., Schenectady, N. Y.

Preparation of High Purity Metals

10:00 A.M.—"High Purity Manganese from Low-Grade Indian Ores" by A. Jogarao, Y. D. Prasada Rao, and S. Gopal, Central Electrochemical Research Institute, Karaikudi, India.

10:30 A.M.—"Melting and Deoxidizing with Atomic Hydrogen" by P. C. Rossin, Research Lab., General Electric Co., Schenectady, N. Y.

11:00 A.M.—"Preliminary Investigation of Hafnium Metal by the Kroll Process" by H. L. Gilbert and M. M. Barr, U. S. Department of the Interior, Bureau of Mines, Albany, Oreg.

11:30 A.M.—"Bomb Reduction of Molybdenum Trioxide by Calcium Metal" by H. L. Gilbert and F. E. Block, U. S. Department of the Interior, Bureau of Mines, Albany, Oreg.

Electrothermics and Metallurgy

Wednesday, May 4, 1955

Electrochemical Techniques in Metallurgical Research (cont'd)
with J. H. Westbrook presiding

Metallography

2:00 P.M.—"Electropolishing from the Viewpoint of Surface Metallurgy" by C. L. Faust, Battelle Memorial Institute, Columbus, Ohio.

2:30 P.M.—"Chemical Polishing of Metallographic Specimens" by H. W. Schadler and J. E. Burke, Research Lab., General Electric Co., Schenectady, N. Y.

3:00 P.M.—"Thermal Etching of Chromium" by M. J. Fraser, D. Caplan, and A. A. Burr, Rensselaer Polytechnic Institute, Troy, N. Y.

Atom Movements

3:30 P.M.—"Segregation Coefficient of Some Group III and Group V Elements in Gold" by E. B. Dale and W. L. Mefferd, Battelle Memorial Institute, Columbus, Ohio.

4:00 P.M.—"The Gray Tin Phenomenon: Additional Data" by R. R. Rogers and J. F. Fydell, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ont., Canada.

4:30 P.M.—"Voltammetry in Fused Salt Systems" by A. J. Kolk, M. E. Sibert, and M. A. Steinberg, Horizons Inc., Cleveland, Ohio.

Industrial Electrolytic

Monday, May 2, 1955

with A. R. Orban presiding

9:15 A.M.—"A New Electrolytic Process for Brine Water by Using a Mercury Jet Cathode" by Shigeru Mizuno and Shinobu Toshima, Tokyo Institute of Technology, Tokyo, Japan.

9:45 A.M.—"Factors Affecting the Formation of Color in Caustic from Diaphragm Chlor-Alkali Cells" by R. E. Cushing, Engineering Dept., Wyandotte Works, Pennsylvania Salt Manufacturing Co., Wyandotte, Mich.

10:15 A.M.—"Technical Analysis of Diaphragm Cells for the Electrolysis of NaCl Solution" by Takashi Mukaibo, Dept. of Applied Chemistry, University of Tokyo, Tokyo, Japan.

10:45 A.M.—"Portable Analyzer for the Determination of Hydrogen and Chlorine in Chlor-Alkali Cell Gas" by R. E. Cushing and R. S. Reichard, Engineering Dept., Wyandotte Works, Pennsylvania Salt Manufacturing Co., Wyandotte, Mich.

11:15 A.M.—"The de Nora Fluent

Amalgam Cell" by Vittorio de Nora, Patrizio Gallone, and Giovanni Trisoglio, Impianti Elettrochimici, Milan, Italy.

11:45 A.M.—"The Influence of Impurities in the Electrolyte in Chlorine-Caustic Electrolysis by the Mercury Cell Process, V. Further Investigation of the Influence of Metals on Cathodic Current Efficiency" by Gösta Angel, Tage Lundén, Stig Dahlerus, and Rolf Brännland, Div. of Applied Electrochemistry, Royal Institute of Technology, Stockholm, Sweden.

Industrial Electrolytic

Monday, May 2, 1955

Round Table
with A. R. Orban presiding

2:00-5:00 P.M.—Round-table discussion on rectifiers. The following companies will be represented: Westinghouse Electric Corp., selenium rectifiers; General Electric Co., germanium rectifiers; ITE, mechanical rectifiers; Allis Chalmers Mfg. Co., mercury arc rectifiers; and Pennsylvania Salt Mfg. Co., rotary converter rectifiers.

Industrial Electrolytic

Tuesday, May 3, 1955

with Warren Sherrow presiding

9:00 A.M.—"The Lithium Industry" by P. E. Landolt, Consulting Engineer, 36 West 44th St., New York, N. Y.

9:25 A.M.—"The Current Efficiency of Fluorine Cells" by J. Dykstra and G. H. Montillon, K-25 Plant, Carbide and Carbon Chemicals Co., Oak Ridge, Tenn.

9:50 A.M.—"Progress of Improvements in Materials of Construction of Fluorine Cells" by J. Dykstra and G. H. Montillon, K-25 Plant, Carbide and Carbon Chemicals Co., Oak Ridge, Tenn.

10:15 A.M.—"New Continuous Processes for Production of Beryllium Hydroxide and Beryllium Metal" by C. W. Schwenzfeier, Jr., Brush Beryllium Co., Cleveland, Ohio.

10:40 A.M.—"Electrochemical Preparation of Boron" by N. F. Murphy, R. S. Tinsley, and G. F. Meenaghan, Dept. of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va.

11:05 A.M.—"Electrolytic Crystal Growth of Titanium" by Q. H. McKenna, M. E. Sibert, and M. A. Steinberg, Horizons Inc., Cleveland, Ohio.

11:30 A.M.—"Electrodeposition of Titanium on Base Metals" by M. E. Sibert and M. A. Steinberg, Horizons Inc., Cleveland, Ohio.

Joint Session
Theoretical Electrochemistry—Industrial Electrolytic

Wednesday, May 4, 1955

Fused Electrolytes
with W. J. Hamer presiding

2:00 P.M.—"Thermodynamics of Fused Electrolytes" by Carl Wagner, Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. (Invited Paper)

2:30 P.M.—"Electrical Conductance and Ionic Migration in Molten Salts" by E. R. Van Artsdalen, I. S. Yaffe, and F. J. Miller, Chemistry Div., Oak Ridge National Lab., Oak Ridge, Tenn.

3:00 P.M.—"Electric Conductance, Transport, and Viscosity in Molten Systems with Special Reference to Molten Silicates and Borates" by J. O'M. Bockris and G. W. Mellors, Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pa. (Invited Paper)

3:30 P.M.—"Transference Numbers of Cations and Anions in Fused Silver Nitrate and Silver Nitrate-Sodium Nitrate Mixtures" by F. R. Duke and Richard Laity, Iowa State College of Agriculture and Mechanic Arts, Ames, Iowa. (Invited Paper)

4:00 P.M.—"Transport Numbers in Pure Fused Thallium(I) Chloride" by Richard Laity and F. R. Duke, Iowa State College of Agriculture and Mechanic Arts, Ames, Iowa.

Joint Session
Theoretical Electrochemistry—Industrial Electrolytic

Thursday, May 5, 1955

Fused Electrolytes (cont'd)
with R. Roberts presiding

9:00 A.M.—"Kinetics of Electrode Processes in Fused Salts" by Paul Delahay, Dept. of Chemistry, Louisiana State University, Baton Rouge, La. (Invited Paper)

9:30 A.M.—"Impedance Measurements at Solid Electrodes in Molten Lithium Chloride-Potassium Chloride" by H. A. Laitinen, Dept. of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill., and R. A. Osteryoung, Dept. of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. (Invited Paper)

10:00 A.M.—"Purification of Lithium Chloride-Potassium Chloride Eutectic as a Polarographic Fused Salt Solvent" by H. A. Laitinen and W. S. Ferguson, Dept. of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill., and R. A. Osteryoung, Dept. of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.

Round Table

10:30 A.M.—Round-table discussion on electrode potentials in fused electrolytes with W. J. Hamer, H. A. Laitinen, and Seymour Senderoff.

Joint Session
Theoretical Electrochemistry—Industrial Electrolytic

Thursday, May 5, 1955

with Allen Russell presiding

2:00 P.M.—"Galvanic Functions of Cells with Molten Salt Electrolytes, I. The Nominal System Mg | KCl-LiCl(1) | Ni" by S. M. Selis, G. R. B. Elliott, and L. P. McGinnis, Diamond Ordnance Fuze Labs., Washington, D. C.

2:25 P.M.—"Galvanic Functions of Cells with Molten Salt Electrolytes, II. The Nominal System Mg | KCl-LiCl-K_2CrO_4(1) | Ni and the Effects of Added Solid Acidic Oxides" by S. M. Selis and L. P. McGinnis, Diamond Ordnance Fuze Labs., Washington, D. C.

2:50 P.M.—"Sodium-Aluminum Equilibria in Cryolite-Alumina Melts" by Morris Feinleib and Bernard Porter, Reduction Research Lab., Kaiser Aluminum and Chemical Corp., Permanente, Calif.

3:15 P.M.—"Electrochemical Characteristics of Melts in the Sb-Sb_2S_3 System" by Tsutomu Yanagase and G. Derge, Metals Research Lab., Carnegie Institute of Technology, Pittsburgh, Pa.

3:40 P.M.—"Liquidus Curves for Aluminum Cell Electrolytes, I. Cryolite-Alumina" by N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, Aluminium Labs., Ltd., Arvida, Que., Canada.

4:05 P.M.—"Liquidus Curves for Aluminum Cell Electrolytes, II. Ternary Systems of Cryolite-Alumina with Aluminum Fluoride, Sodium Fluoride, and Sodium Chloride" by N. W. F. Phillips, R. H. Singleton,

and E. A. Hollingshead, Aluminium Labs., Ltd., Arvida, Que., Canada.

Theoretical Electrochemistry

Monday, May 2, 1955

with Ernest Yeager presiding

9:15 A.M.—"Concentration Polarization and Overvoltage" by C. V. King, Dept. of Chemistry, New York University, New York, N. Y.

9:40 A.M.—"Ion Distribution during Electrolysis" by H. P. Dengler and H. B. Linford, Dept. of Chemical Engineering, Columbia University, New York, N. Y.

10:05 A.M.—"Fundamental Thermodynamics and Kinetics of Electrode Processes" by Pierre Van Rysselberghe, Dept. of Chemistry, University of Oregon, Eugene, Oreg.

10:30 A.M.—"Some Applications of the Thermodynamics of Irreversible Electrochemical Processes" by Pierre Van Rysselberghe, Dept. of Chemistry, University of Oregon, Eugene, Oreg.

10:55 A.M.—"Elucidation of the True Mechanism of Hydrogen Evolution, I. Quantitative New Consecutive Theory on Smooth Platinum Electrode" by A. M. Azzam, Chemistry Dept., Faculty of Science, Ein-Shams University, Cairo, Egypt.

11:20 A.M.—"Mechanisms of Hydrogen Producing Reactions on Palladium" by J. P. Hoare and Sigmund Schuldiner, Naval Research Lab., Washington, D. C.

Theoretical Electrochemistry

Monday, May 2, 1955

with Paul Delahay presiding

2:00 P.M.—"Hydrogen Overpotential on Silver Single Crystals" by H. B. Morley and F. E. W. Wetmore, Electrochemical Lab., University of Toronto, Toronto, Ont., Canada.

2:25 P.M.—"Hydrogen Overpotential Studies on Aluminum" by D. J. Hansen and F. E. W. Wetmore, Electrochemical Lab., University of Toronto, Toronto, Ont., Canada.

2:50 P.M.—"Calculation of the Effect of Cationic Specific Adsorption on the Proton Discharge Rates at Mercury and Other Cathodes" by B. E. Conway, J. O'M. Bockris, and B. Lovrocek, Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pa.

3:15 P.M.—"The Inference of Adsorption from Double Layer Capacitance Measurements" by B. H. Clampitt and R. S. Hansen, Ames Lab., U. S. Atomic Energy Commission, Ames, Iowa.

3:40 P.M.—"The Kinetics of the Oxygen Electrode on Active Carbon" by Myron Davies, Milton Clark, Ernest Yeager, and Frank Hovorka, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio.

4:05 P.M.—"Dissolution of Metals in Acids, III. Kinetics" by A. C. Makrides, Institute for the Study of Metals, University of Chicago, Chicago, Ill.

4:30 P.M.—"Anodic Polarization of Titanium in Nonaqueous Base Etching Solutions" by Morris Eisenberg and R. E. De La Rue, Stanford Research Institute, Stanford, Calif.

Theoretical Electrochemistry

Tuesday, May 3, 1955

with Ernest Yeager presiding

9:00 A.M.—"Oxide Film Formation on the Surface of Metals in Aqueous Solutions and the Evaluation of Their Standard Potentials, III. The Lead Electrode" by S. E. S. El Wakkad and T. M. Salem, University of Pennsylvania, Philadelphia, Pa., and Cairo University, Cairo, Egypt.

9:25 A.M.—"Anodic Oxidation of Zinc and Zinc-Tin Alloys at Very Low Current Density" by S. E. S. El Wakkad, A. M. Shams Eldin, and H. Kotb, University of Pennsylvania, Philadelphia, Pa., and Cairo University, Cairo, Egypt.

9:50 A.M.—"Anodic Oxidation of Metal Ions to Insoluble Higher Oxides with Special Reference to Manganese Dioxide" by H. K. Chakrabarti and T. Banerjee, National Metallurgical Lab., Council of Scientific and Industrial Research, Jemshedpur, India.

10:15 A.M.—"The Kinetics of Formation of Anodic Ta_2O_5: Further Studies" by D. A. Vermilyea, Metallurgy Research Dept., Research Lab., General Electric Co., Schenectady, N. Y.

10:40 A.M.—"Mathematical Studies of Galvanic Corrosion, II. Coplanar Electrodes with One Electrode Infinitely Large and with Equal Polarization Parameters" by J. T. Waber and Marshall Rosenbluth, University of California, Los Alamos Scientific Lab., Los Alamos, N. Mex.

11:05 A.M.—"Mathematical Studies of Galvanic Corrosion, III. Semi-Infinite Coplanar Electrodes with Equal Constant Polarization Parameters" by J. T. Waber, University of California, Los Alamos Scientific Lab., Los Alamos, N. Mex.

Theoretical Electrochemistry

Tuesday, May 3, 1955

with Ralph Roberts presiding

2:00 P.M.—"Mathematical Studies on Galvanic Corrosion, IV. Influence of Electrolyte Thickness on the Potential and Current Distributions over Coplanar Electrodes Using Polarization Parameters" by J. T. Waber and Bertha Fagan, University of California, Los Alamos Scientific Lab., Los Alamos, N. Mex.

2:25 P.M.—"Polar Properties of Solvent and the Conductance of Electrolytes at Infinite Dilution" by E. S. Amis, Dept. of Chemistry, University of Arkansas, Fayetteville, Ark.

2:50 P.M.—"The Heat of Hydration of Metallic Ions" by A. L. Bisio, Dept. of Chemical Engineering, Columbia University, New York, N. Y.

3:15 P.M.—"Conductances, Viscosities, and Densities of Solutions of Potassium Thiocyanate in Methanol at Temperatures within the Range 25°–50°C" by P. G. Sears, R. R. Holmes, and L. R. Dawson, Dept. of Chemistry, University of Kentucky, Lexington, Ky.

3:40 P.M.—"The Conductance of Lithium Bromide at Low Concentrations in Methanol within the Temperature Range 20° to −50°C" by P. G. Sears, R. L. McNeer, and L. R. Dawson, Dept. of Chemistry, University of Kentucky, Lexington, Ky.

4:05 P.M.—"Conductimetric and Viscometric Behavior of Lithium Bromide in 50-50 Weight Per Cent Methanol-Acetone at Temperatures within the Range 20° to −50°C" by L. R. Dawson, R. A. Hagstrom, and P. G. Sears, Dept. of Chemistry, University of Kentucky, Lexington, Ky.

4:30 P.M.—"Conductances of Some Moderately Concentrated Solutions of Metallic Perchlorates in the Mixed Solvent Methanol-Acetone at Low Temperatures" by P. G. Sears, W. W. Wharton, and L. R. Dawson, Dept. of Chemistry, University of Kentucky, Lexington, Ky.

Theoretical Electrochemistry

Wednesday, May 4, 1955

with C. V. King presiding

9:00 A.M.—"Electrolytes of Binary

Solutes in Ketones" by J. E. Lilienfeld, H. Y. Hsiao, and H. S. Myers, Power Condenser and Electronics Corp., Washington, D. C.

9:25 A.M.—"The Electrochemistry of Some Nonaqueous Solutions of Inorganic Salts" by M. C. Henry, W. M. McNabb, and J. F. Hazel, Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pa.

9:50 A.M.—"Conductivities of Random Dispersions" by R. E. De La Rue and C. W. Tobias, Dept. of Chemistry and Chemical Engineering, University of California, Berkeley, Calif.

10:15 A.M.—"Quantitative Measurements of Colloidal Vibration Potentials" by Ernest Yeager, Joseph Dereska, and Frank Hovorka, Dept. of Chemistry, Western Reserve University, Cleveland, Ohio.

10:40 A.M.—"Electrokinetic Potentials of Bulk Metals from Streaming Currents" by R. M. Hurd and Norman Hackerman, Defense Research Lab. and Dept. of Chemistry, University of Texas, Austin, Texas.

11:05 A.M.—"High Pressure Oxidation of Metals; Oxidation of Metals under Conditions of a Linear Temperature Increase" by J. P. Baur, D. W. Bridges, and W. M. Fassell, Jr., Dept. of Metallurgy, University of Utah, Salt Lake City, Utah.

Highlights of the Board of Directors' Meeting

(Held January 21, 1955)

The President announced that Professor H. H. Uhlig, of Massachusetts Institute of Technology, has been elected President; Sherlock Swann, Jr., of the University of Illinois, Third Vice-President; and L. I. Gilbertson, of Air Reduction, Inc., is Treasurer.

The following budget was approved for the operation of the Society for 1955:

BUDGET FOR 1955

Income

	1954 Estimated	1954 Actual	1955 Estimated
Membership Dues	$32,400	$29,546	$30,000
Sustaining Memberships	9,000	10,285	10,000
Sale of publications			
Back Transactions	800	242	100
Reprints & Preprints	3,000	2,789	3,000
Nonmember Journal Subscriptions	18,000	22,548	25,000
Office Sale of Journal	1,500	459	500
Royalties "Cathodic Protection"	200	375	200
Convention Registration (net)	300	652	1,500
Advertising	15,000*	16,517*	16,500*
	$80,200	$83,413	$86,800

Expenditures

Printing & Mailing Journal	$28,000*	$27,731*	$31,000*
Reprints	2,500	2,491	2,500
Publication Committee	250	231	250
Advertising Commission	5,200*	5,200	5,200*
ABC Rating	300	798	1,000
Salaries	34,000	34,276	35,500
Rent	2,400	2,400	2,400
Postage, Supplies, Misc.	6,200	5,914	6,200
Auditor	175	175	175
Local Sections & Divisions	1,000	698	1,000
Young Author's Prize	100	100	100
	$80,125	$80,014	$85,325

Summary

Income	$80,200	$83,413	$86,800
Expenditures	80,125	80,014	85,325
Excess Income Over Expenditures	$ 75	$ 3,399	$ 1,475

* These items to be increased for reasons explained on Budget approved by Board of Directors, January 30, 1953.

At the request of the Secretary, the Ways and Means Committee was given the job of studying sick leave policy and setting up job classifications and salary brackets for the national office.

The President reported that he had recently visited the Chicago, Cleveland, and Niagara Falls Sections, and had communications with the Philadelphia Section. All these sections are showing great interest in the affairs of the national organization, particularly with respect to handling of national conventions.

The problem of the program booklet was discussed at some length, and this matter was referred to the Ways and Means Committee for study along with all the other factors involved in the financing of national meetings.

The Bylaws of the Industrial Electrolytic Division were approved, as were the new Bylaws for the Society, which were published in the March issue of the JOURNAL (Vol. 102, p. 60C).

Dr. R. H. Price, from the University of Cincinnati, gave a brief statement of plans for the Cincinnati Meeting.

The Secretary announced that the date for the Houston Meeting had been changed from the spring of 1961 to the fall of 1960, and the local committee is starting to work on that meeting.

Mrs. R. G. Sterns reported that 8 papers have been scheduled for the January and February JOURNAL, and 9 for March and April, making a total of 34 papers. For the May and subsequent issues 27 papers are awaiting publication. There are 46 manuscripts being reviewed and 14 are now in the hands of authors for revision. It is hoped that the increased budget for printing and mailing of the JOURNAL will reduce this backlog.

The Corrosion Handbook Committee

recommended the discontinuance of the Prize Essay Contest for this year. This was approved.

The meeting was adjourned at 4:00 P.M.

HENRY B. LINFORD, *Secretary*

DIVISION NEWS

Electronics Division

The Committee on Bylaws (A. P. Thompson, H. R. Harner, and J. R. Musgrave) recommends the following revisions. These revisions will be voted on at the annual meeting of the Division during the Cincinnati Convention.

Article I, Section 2

Change to:

The Electronics Division shall consist of three groups:

a. General Electronics
b. Luminescence
c. Semiconductors

(Note: With the admission of the Semiconductor group in 1954, provision is being made for their place in our organization.)

Article II, Section 2

Change (in paragraph 6) to:

All funds . . . shall be dispensed only in accordance with Article V, Section 3b of these Bylaws.

(Note: Correction of typographical error.)

Article III, Section 1

Change to:

The officers of the Division shall be a Chairman, the Group Chairmen, and a Secretary-Treasurer.

(Note: Change made only for clarification.)

Article IV, Section 2

(Note: Several changes are suggested for clarification. None of the changes affects the previous provisions.)

Change 1st paragraph to: (last two lines)

"Shall make nominations subject to the following rules".

Change paragraph c to:

"The report of the nominating committee shall be made to the officers"

Change paragraph d (last two lines) to:

"before the elections in order that the provisions of Article IV, Section 2-a may be complied with".

Article VI, Section 1

Change Section 1 to:

"The governing body of the Division shall be an Executive Committee consisting of seven (7) or more members. The officers, the representative of the Division on the Membership Committee of the Society, the representatives selected by the Publication Committee of the Society to represent the Division, the editor of the Semiconductor Digest, and the most recent past Division Chairman shall constitute the Executive Committee. No member of the Executive Committee may have more than one vote."

(Note: The change here suggests dropping symposia chairman from the Executive Committee. The reduction in size will make a more workable committee.)

Article VII, Section 1

Change to:

The Division shall hold one business meeting annually, presided over by Division officers . . . following a symposium program.

(Note: This change allows the officers to select an appropriate day for the meeting. Heretofore they were limited to certain days by the old Bylaws.)

Article VII, Section 2

Change to:

The Division shall hold symposia on Electronics, Luminescence, and/or Semiconductors once a year, preferably at the Spring Convention."

(Note: Changes made to reflect wider scope of our activities.)

Article VII, Section 3

Change last sentence to:

"The Chairman . . . may elect to conduct by mail such business. . . ."

(Note: Change made for clarification only.)

The Nominating Committee (R. H. Cherry, Chairman, G. E. Crosby, and M. Sadowsky) has selected the following nominees for officers during the 1955–1956 term:

Chairman—Charles W. Jerome (Sylvania Electric Products Inc., Salem, Mass.)

Vice-Chairman (Luminescence)—J. H. Schulman (Naval Research Laboratory, Washington, D. C.)

Vice-Chairman (General Electronics)—C. Dichter (General Electric Co., Syracuse, N. Y.)

**Vice-Chairman (Semiconductors)*—F. J. Biondi (Bell Telephone Labs., Murray Hill, N. J.)

Secretary-Treasurer (3-year term)—Martin F. Quaely (Westinghouse Electric Corp., Bloomfield, N. J.)

Each nominee has given assurance of his willingness to serve if elected.

The Bylaws of the Division provide that additional nominations may be made by petition signed by 5 members of the Division. Such petitions must be in the hands of the Nominating Committee before the election and the nominees must have given assurance of their willingness to serve if elected.

The election will be held at the business meeting of the Electronics Division during the Spring Meeting of the Society in Cincinnati.

C. W. JEROME, *Secretary-Treasurer*

Oxide Cathode Symposium

In line with its attempts to provide media for free exchange of experiences in the more practical and materialistic sides of the field of electronically active solid devices, components, and parts, the Electronics Division, under the Chairmanship of Dr. C. P. Hadley of RCA, is sponsoring a symposium on oxide cathodes this year.

Dr. W. B. Nottingham, who is well known to all workers in the field of thermionic emission, will deliver the keynote address for this symposium. His subject will be "Fundamental Phenomena of Thermionic Emission." The symposium will consist of two full sessions devoted to papers covering:

1. Preparation and fabrication of electronically active materials and cathodes.

2. Properties of alkaline earth oxides and also properties of base material, the interface, the coating proper, and the cathode as a whole in conventional coated cathodes.

3. Influences on the properties of cathodes as a function of environment, including considerations of poisoning phenomena, life expectancy, peeling, etc.

4. Thermionic emitters such as L-cathodes, impregnated cathodes, molded cathodes, matrix cathodes, etc.

All who are interested in a more practical side of oxide cathodes are invited to attend this symposium.

A. E. MIDDLETON, *Vice-Chairman (General Electronics)*

* Provisional nomination pending formal activation of the Semiconductor Group at the annual meeting.

Electronics "Enlarged Abstracts" Available

The Electronics Division of the Society will again publish an "Enlarged Abstracts" booklet for the Spring 1955 convention of the Society at Cincinnati. The booklet will have 1000-word abstracts of the papers to be presented before the Electronics Division in its symposia on: Luminescence; Semiconductors; Phosphor Application; Oxide Cathodes. The abstracts will contain pertinent information and experimental data given in the papers and will provide these details before publication, thus aiding workers in the field. The abstracts will be "printed but not published."

The abstract booklets should be available about April 18th; the price will be $2.00. Orders should be sent to: Charles W. Jerome, 60 Boston St., Salem, Mass. Booklets will also be available at the Cincinnati Meeting.

Semiconductor Book Available

Under the sponsorship of the Society, a book, compiled by Battelle Memorial Institute, "Abstracts of the Literature on Semiconducting and Luminescent Materials and Their Applications, 1953 Issue" is being published by John Wiley & Sons, Inc.

Members of the Society who wish to purchase the book, to be sold for $5.00, at the 33⅓% member discount should send their orders to Society Headquarters, 216 West 102nd St., New York 25, N. Y. The Society will forward orders to John Wiley & Sons, Inc., who will ship the volume with the invoice. In order to receive the member discount, *orders must* be sent to Society Headquarters.

Electrothermics and Metallurgy Division

The following men were appointed to the Nominating Committee of the Electrothermics and Metallurgy Division by I. E. Campbell, Division Chairman:

B. W. Gonser, *Chairman*
A. T. Hinckley
C. P. Zergiebel

Their recommendations for Division officers for 1955–1957 are:

Chairman—A. C. Haskell, Jr.
Vice-Chairman—A. U. Seybolt
Vice-Chairman—G. M. Butler
Secretary-Treasurer—E. M. Sherwood
Members-at-Large—John C. McMullen, Gary Steven, Marvin J. Udy, J. H. Westbrook, and I. E. Campbell.

A. C. Haskell, Jr.,
Secretary-Treasurer

Theoretical "Enlarged Abstracts" Available

The Theoretical Electrochemistry Division is publishing for the first time enlarged abstracts of papers to be presented at its symposia at the Cincinnati Meeting of the Society. The booklet will also include abstracts of the Fused Electrolytes Symposia sponsored jointly by the Theoretical Electrochemistry and Industrial Electrolytic Divisions. Copies of the "Enlarged Abstracts" will be available after April 15 at $2.00 each from Professor Ernest Yeager, Department of Chemistry, Western Reserve University, Cleveland 6, Ohio, and will be on sale at the Registration Desk at the Cincinnati Meeting.

SECTION NEWS

Chicago Section

Two speakers addressed the Chicago Section on February 4, 1955. Mr. G. H. Didinger of the National Carbon Company described many new applications for batteries which have been developing or can be expected. Mr. Bernard Ross of the National Semiconductor Products Company discussed "Semiconductor Batteries."

Mr. Didinger described many new applications for dry cells. Sometimes these involved the use of existing types of batteries, and sometimes a development of entirely new batteries to meet new requirements. High-current dry cells are required for photoflash bulbs. There are different requirements for electronic flashing tubes which are xenon filled. One interesting application of a tiny battery is to provide the power to wind watches automatically. Special instruments such as geiger counters frequently have demand for constant voltage batteries. Hearing aids have been producing requirements for new miniature batteries.

In general, transistor circuits offer new markets for several kinds of batteries. Their low power requirements make possible the use of batteries for powering such circuits for doing many things which previously required plug-in power. Telephone companies are adding many carriers and repeaters in their lines for a large-scale market. There are many radio receivers which would be useful as portable instruments. They could, for example, be carried by soldiers, policemen, workmen on special jobs, etc.

In addition, there are undoubtedly applications for batteries which have not yet been developed. There has recently been talk of portable television sets. These would be battery powered. Of course, to make them practical a substitute is requred for the kinescope tube.

Mr. Ross described the two general types of semiconductors and some of the properties of the junction which can be made between opposite types. He likened the junction between *n* and *p* semiconductors to that between cathodic and anodic materials in solution.

Several interesting applications of such junctions were described, and some speculation was made concerning the use of such things for power. It was pointed out that light quanta can cause a current to flow from such a semiconductor battery. Bombardment by nuclear disintegrations will similarly create currents in this fashion. Efficiencies of the order of 10% have apparently been obtained by the Bell Telephone Laboratory in the production of electrical power from sunlight. Junctions which can be used in this way are made of single crystals of silicon with boron diffused into the surface layers.

Some discussion was given on some of the problems involved in making practical power producing junctions, and some applications for small power sources were described.

Joseph E. Draley, *Secretary*

New York Metropolitan Section

The speaker for the January 12th meeting of the New York Metropolitan Section was Dr. Erwin W. Müller, Professor of Physics, Pennsylvania State University. He designed the electron microscope in 1936, but had little opportunity to make use of it until after the war. He developed it further in Germany after the war, and is continuing his research on field emission at Pennsylvania State University.

Dr. Müller opened his talk by explaining that the world in which he is working takes in an area as small as

the point of a needle. The emission microscope consists of the emitting electrode which is tapered to a sharp point, an anode in the form of a ring, and, beyond that, a screen. A filament located in a side-arm may be used to evaporate metals or other substances to form a coating on the cathode. The point of the cathode may be formed by etching or electropolishing. Such a surface is then comparatively rough, but on heating the metal close to its melting point, surface migration smooths the surface. The emitting surface at the point of the needles is curved rather than flat. The tube is baked out and evacuated to a pressure of about 10^{-11} mm of mercury with the aid of getters. When a potential of the order of 30 million v/cm is applied, electrons leave the point in straight lines and the electron beam of very short wave length (10^{-5} cm) forms a picture on the screen which can be photographed. The amount of magnification is dependent on the distance from the cathode to the screen and the shape of the emitting tip. The resolution of the microscope limits the magnification which it is practical to use. A beam of electrons leaving a point takes the form of a parabola, so that the point shows on the screen as a disc. The resolution is of the order of 15 to 20 Å, or about the same as that of the electron microscope.

Dr. Müller described a number of experiments he has carried out with the field emission microscope and showed slides of pictures taken. A most interesting movie of the changes taking place on the sample was also shown. By use of this microscope it is possible to study the work function of different crystal planes and to study emission at different temperatures. It has been shown for the first time that different planes of a given crystal do have different work functions. Cathodes of tungsten and molybdenum have been used. When other metals are evaporated onto the cathode, they are first deposited on the side toward the filament. By heating the cathode the film migrates around the point, and when the film is only a fraction of a monolayer it is distributed preferentially on certain crystal planes. When a molybdenum cathode with a film of cesium was heated, the cesium which remained was on the planes that normally do not emit. The field emission-microscope might be used to study hot strength. At 700°C and under a strong field a molybdenum cathode deforms, but if silicon has been deposited and the silicide formed there is no deformation under these conditions.

Oxide films have been studied by means of field emission microscopy, including the absorption and desorption of oxygen as a function of temperature. Oxygen at a pressure of 10^{-8} mm of mercury is sufficient to form a film, and at a pressure of 10^{-6} mm a layer is built in two seconds. In order to study two metals simultaneously, two tubes, one with a tungsten cathode and one with a molybdenum cathode, were connected together. When oxygen was admitted to the system a film formed immediately on the tungsten, but some time elapsed before a film started to form on the molybdenum. Once started, the film formed rapidly. If a slight film originally existed on both metals, the film on the molybdenum grew as rapidly as that on the tungsten. It is possible to see on which crystallographic plane the oxide films form first.

A monolayer of nitrogen can be formed on both tungsten and molybdenum, and the rate of formation is the same on both metals. Oxygen will replace nitrogen; this happens at once on tungsten but some time is required to initiate the replacement on molybdenum. When carbon is deposited on molybdenum, and heated, a carbide lattice is formed. Further heating causes the carbon to be absorbed into the metal, and finally to be removed by evaporation.

Dr. Müller believed that the resolution of the microscope was such that he should be able to see a large molecule such as is found in many organic compounds. Phthalocyanide was selected because it is a stable compound which could be evaporated without decomposition. When less than a monolayer of this compound had been deposited on the cathode, the individual molecules could be seen. The cathode was bombarded with copper or gas ions. These particles did not have enough energy to dislodge a molecule of phthalocyanide, but did cause the molecule to move when struck and its movement could be followed on the screen. When the cathode is heated the phthalocyanide evaporates and molecules can be seen to disappear from the field. Barium crystals can be formed on tungsten or molybdenum cathodes. When these crystals are evaporated slowly they do not disappear at once as do molecules of phthalocyanide, but shrink and finally disappear.

When a barium coated electrode tip was made positive, at a voltage of 100 million v/cm nothing happened, but when the voltage was raised to 120 million, barium was torn off the tip. Thorium could be torn off the tip with a field of 240 million v/cm. The field had to be raised to 340 million v to remove all the thorium. A picture could be taken when absorbed hydrogen was removed from the electrode as ions. In this way a resolution of 5 Å could be obtained. When helium was used instead of hydrogen, pictures could be taken with a field of 340 million v and a resolution of 4 Å. When the field was raised to 400 million volts, the tungsten lattice was deformed and monolayers of tungsten removed. The formal talk was followed by a discussion period.

Dr. Müller suggested that field emission might well be used in a mass spectrometer. Gas molecules are ionized some distance from the tip of the cathode by the stream of electrons, so that large molecules are not cracked by contact with a hot cathode.

KENNETH B. MCCAIN,
Secretary-Treasurer

Ontario-Quebec Section

The second meeting of the Ontario-Quebec Section was held at McGill University in Montreal on Friday, January 28, 1955. There was an excellent attendance of 60 members, students, and friends of the Society.

Professor J. U. MacEwan of McGill acted as technical chairman and introduced our two speakers, Mr. Jan. H. Reimers, M.B.E., Consulting Metallurgist of Toronto, and Mr. Joseph C. Bischoff, Works Metallurgist of the International Nickel Company, Copper Cliff, Ontario.

Mr. Reimers gave an excellent and informative paper on "Electric Smelting of Sulfide Ores," with most particular reference to the smelting of copper ores. He described the types of furnaces employed in Scandinavian practice, outlining the advantages and disadvantages of each. Mr. Reimers' figures on the low slag losses possible through electric smelting were most interesting. He stressed that the applicability of electric furnace smelting for recovery of copper from ores as against chemical recovery means was a question of economics, but that it would appear that electric smelting had a future in Canada due to the remoteness of new large-scale deposits of ore and their closeness to large hydroelectric resources ready for harnessing.

Mr. Bischoff gave a most complete and documented paper on the development and use of the three-phase arc furnace for the melting and recasting of cathode copper. He described the development work done by Inco and the several furnaces now used in Canada and the U.S.A. Mr. Bischoff showed that the electric furnace has great technical and economic advantages over the reverberatory furnace for this purpose.

Each paper was followed by a question period. The large number of questions capably handled by our speakers testified to the interest of their audience.

JOHN SUMNER, *Secretary-Treasurer*

Washington-Baltimore Section

Synthesis of Electric Insulation by Means of Gamma Radiation was the topic presented by Mr. T. D. Callinan of the U. S. Naval Research Laboratory at the January 20th meeting of the Section held at the National Bureau of Standards. Presenting his remarks from a chemist's viewpoint, the speaker described the use of gamma radiation to effect well known chemical reactions—the polymerization of monomers. Classically these reactions require catalysts and/or heat, but gamma rays also cause polymerization by the mechanism of free radical formation. The radiation may be selected so that its energy is sufficient to remove electrons from the atomic orbits, but not sufficient to cause nuclear reactions. Mr. Callinan described some of the factors considered in selecting the radiation source, and the experimental techniques. He stressed that this was not a new chemistry but a new energy source: the mechanisms of chemical reactions are unchanged, and overall kinetics may or may not be changed as a result of increasing the rate of free radical formation.

The gamma radiation source in the work described was Co^{60} contained in sealed tubes of stainless steel. These were arranged to suit the geometry of the experiment and the monomer exposed to the radiation for varying lengths of time. The reaction was carried out at the bottom of a well of water that acted as a radiation shield. The reaction mixtures sealed in steel boxes were lowered into the field through the water barrier.

The properties of gamma polymerized materials are often different from those produced by conventional methods. There are frequently differences in color, specific gravity, molecular weight, tensile strength, and deformation temperature or melting point. Frequently these differences extend the usefulness of the polymer as, for instance, an increase in the deformation temperature may render a "gamma" polymer useful where the conventional product would soften and distort.

Gamma radiation has also been used to produce copolymers that have unique physical characteristics, and Mr. Callinan expressed the belief that a gamma polymer or copolymer will be tailored to fit each new use as it develops.

Color photographs of polyethylene, polystyrene, polysilicone elastomer, and copolymers of acrylonitrile and methyl acrylate augmented the data presented describing these interesting materials. A discussion period concluded the meeting.

JEANNE BURBANK, *Secretary-Treasurer*

The regular monthly meeting of the Section was held on February 17 at the National Bureau of Standards. The speaker of the evening was Dr. Allen S. Russell, Chief of the Physical Chemistry Division of The Aluminum Company of America. Dr. Russell's topic was the Mechanism of the Electrolysis of Alumina—A Sixty Year Old Mystery.

The commercial procedure for the electrowinning of aluminum metal from a molten cryolite solution of alumina was described. Such a process poses many questions and the nature of the ionic species is one of the most intriguing. In his talk Dr. Russell described the postulations that have been offered to explain the deposition of sodium and aluminum at the two electrodes. A great variety of complex ions may be envisioned as present in such a system. It was to solve this question that intensive investigations of the electrolyte have been undertaken.

Dr. Russell described the numerous problems facing the chemist when he tries to reconcile the experimental data for the solution, alumina in molten cryolite. The results from density and conductivity measurements, freezing point lowering, viscosity and its temperature coefficient, and transference measurements have all combined to emphasize the complexity of the problem. The cell reaction itself may be written in several ways, none of which is decidedly preferable at the present stage of our knowledge.

At the conclusion of the talk, there was an animated discussion period followed by a coffee hour.

JEANNE BURBANK, *Secretary-Treasurer*

NEWS ITEMS

M.I.T. Electrochemistry Colloquium

Massachusetts Institute of Technology is offering an Electrochemistry Colloquium sponsored by the Departments of Metallurgy and Chemistry. The Colloquium, which began February 15, will run through May 17. Part of the program is listed below.

April 5—Effect of Electrical Double Layer on Oxidation of Metals, Professor H. H. Uhlig, Department of Metallurgy, M.I.T.

April 12—Ion Exchanger Electrodes, Professor George Scatchard, Department of Chemistry, M.I.T.

April 19—Electrochemical Applications of Ion Exchange Membranes, Dr. W. J. Juda, Ionics, Inc., Cambridge, Mass.

April 26—Applications of Polarization Measurements to Corrosion, Mr. Roger A. Covert, Department of Metallurgy, M.I.T.

May 10—Adsorption Studies at Silver Salt-Solution Interfaces, Mr. W. J. Freyberger, Department of Metallurgy, M.I.T.

May 17—Fuel Cells, Mr. George W. Heise, Cleveland, Ohio.

Copies of the program may be obtained from Mrs. J. Menefee, Dept. of Metallurgy, Rm. 8–202, Massachusetts Institute of Technology, Cambridge 39, Mass.

NACE Committee to Study Prefabricated Plastic Films

Organization of a new Technical Unit Committee, whose objective will be to define certain minimum standards of film formulation and application, has been announced by the National Association of Corrosion Engineers. R. B. Bender, Plastic Engineering & Sales Corp., Fort Worth, Texas, is chairman of the committee designated T-2K on Prefabricated Plastic Film for Application to Pipe Lines. The first meeting was during the 11th Annual NACE Conference and Exhibition, March 7–11 in Chicago.

Specific objectives of the committee are to study bonding agents or adhe-

sives, prefabricated plastic films presently available and as discovered in the laboratory, proper applications of both pressure sensitive and prefabricated films to pipelines, and preparation of a history of experience and results obtained from use of prefabricated films.

Monmouth College Essay Contest

Professor G. W. Thiessen, Chairman of the Department of Chemistry at Monmouth College, Monmouth, Ill., is sponsoring an essay contest at Monmouth on the subject of "Electrode Potentials," and personally is offering a $5.00 prize to the winner. A colleague of his from Augustana College will judge the entries.

Professor Thiessen's establishment of the contest was inspired by the national Prize Essay Contest of The Electrochemical Society which met with considerable response and success among his students. The Society's contest for 1955 has been discontinued upon recommendation of its Corrosion Handbook Committee. Professor Thiessen has expressed his desire to see it continued.

Bell Labs. Develops Unique Machine

A machine that can automatically carry out a series of more than 15 intricate steps in making experimental transistors—the solid pea-sized amplifiers that have most of the advantages of vacuum tubes—is now in an early stage of development at Bell Telephone Laboratories.

The unique machine, familiarly known as "Mr. Meticulous," will, in less than one minute, take a tiny bar of a special semiconducting material, such as germanium or silicon—a bar almost as thin as a human hair—examine it carefully for electrical characteristics, and accept or reject it. If it accepts it, the machine fixes a fine gold wire to a critical point on the bar within an accuracy of $\frac{1}{20,000}$ of an inch. Then, still within one minute, it connects this wire to one of the four wires leading out of the transistor, flips the bar end over end, repeats the entire operation with another wire on the opposite side, and finally runs a series of electrical tests on the completed transistor.

Transistors for research purposes must be of the highest precision and accuracy. When fashioned by human hands over any extended period of time, some transistors are produced which are substandard and useless for research purposes. This is the result of fatigue on the part of the technician. But "Mr. Meticulous" never gets tired, never loses his precision or accuracy. His hand never shakes and his highly organized electronic "brain" rarely has mental lapses.

The machine, originated by R. L. Wallace of Bell Telephone Laboratories, where the transistor was invented, may someday be a pilot model for industrial machines to be used in assembly-line transistor manufacture. At this stage, however, "Mr. Meticulous" is primarily a laboratory device designed to aid research on so-called "junction" transistors.

Pittsburgh Meeting Abstract Deadline

Triplicate copies of abstracts of papers to be scheduled for presentation at the Pittsburgh Meeting of the Society, October 9 to 13, 1955, must reach the Secretary's office, 216 West 102nd Street, New York 25, N. Y., not later than *June 15, 1955* in order to be included in the program.

Sessions will be scheduled on: Batteries, Corrosion, Electrodeposition, Electro-Organics, and Electrothermics and Metallurgy.

Triplicate copies of abstracts of papers for the Spring Meeting of the Society in San Francisco, April 29 to May 3, 1956, must reach the Secretary's office not later than January 2, 1956.

Sessions probably will be scheduled on: Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

Triplicate copies of manuscripts are acceptable either before or after presentation of a paper at a meeting. There is no connection between presentation of papers and publication in the JOURNAL.

Pennsalt Acquires Interest in Index Chemical Co.

The Pennsylvania Salt Manufacturing Company has acquired a major interest in the Index Chemical Company of Houston, Texas, Pennsalt President George B. Beitzel has announced.

Index, first in the United States to produce ethyl and methyl mercaptans synthetically for commercial sale, also produces dimethyl and diethyl sulfides. These organic sulfur compounds are used principally as gas odorants and as intermediates for agricultural chemicals, animal feed supplements, pharmaceuticals, and solvents.

Index activities will be integrated with the production and sales departments of Sharples Chemicals Inc., a Pennsalt subsidiary and pioneer producer of related synthetic organic sulfur compounds. By combined utilization of Index processes, Sharples' market development and sales organizations, and Pennsalt's Whitemarsh Research staff, the company hopes to realize greater production and distribution of these and similar compounds.

New Enthone Discovery

Successful results with a powder—it looks like flour—that speeds the action of acids for dissolving defective chromium and nickel from copper base metals without injuring the base metals were disclosed today by Enthone, Inc., of New Haven, leaders in the metal finishing industry.

The announcement was made shortly after the receipt of a patent issued to the inventor, Dr. Walter R. Meyer, President of Enthone. The invention was hailed as a major discovery in the general metal manufacturing industry. Although a well-kept secret from the general public until today, the powder and new process have already saved millions of dollars worth of reclaimed parts for scores of national manufacturers.

Dr. Meyer said that this invention, the 10th he has had patented, covers a process and product for rapid dissolving of defective chromium, nickel, and other plates from copper, brass, and other copper base metals without attacking the base metal. Until now, he explained, all existing processes for dissolving nickel and chromium injured the base metal usually so badly that it required extensive labor to refinish the part. And frequently, he added, the part was destroyed beyond repair during the stripping action, all costly to industrialists. "The new process," he said, "makes it possible to dissolve metals without hurting the base metal and leaves a clean, smooth surface, ready for refinishing. All types of industries have been using it successfully," he continued, "including manufacturers of radio and electronic equipment, household appliances, cameras, office and business machinery, and automobile parts."

The process was developed in the Enthone, Inc., laboratories, where extensive research is being conducted daily on scores of unsolved problems

in the metal finishing industry. The results of these research efforts have improved methods of plating, provided better finishes for metal products, and saved large sums of money for the general metal manufacturing industry.

The new patent, U.S. Pat. No. 2,698,-781, issued January 4, 1955, is titled "Accelerating Action of Acids on Metals." The products sold under the patent are designated on the market as Enstrips "S" and 1658. Enthone, Inc., has offices and warehouses in principal cities of the United States, Europe, and South America.

"This product is furnished as a dry powder that is added to certain acids which increases the rate of dissolving the acids on nickel and chromium thousands fold," stated Dr. Meyer. "Whereas the acid without the powder may dissolve the nickel or chromium in a matter of hours, the addition of the powder enables dissolving of the defective coatings in a matter of seconds or minutes. In addition, the base metal is left unharmed."

The combination of this latest invention with a prior one by Dr. Meyer and Dr. Richard C. Springer of Germany, which has enabled the rapid stripping of nickel, chromium, and other metals from steel bases without attacking the base metal, now makes it possible to solve almost any metal stripping problem.

Union Carbide Scholarships

Sixty-eight more Union Carbide Scholarships will go into effect in the fall of 1955 at 11 additional colleges and universities according to a recent announcement made by A. V. Wilker, Trustee, The Union Carbide Educational Fund, and former vice-president, Union Carbide and Carbon Corporation.

This new allocation of scholarships marks the first time, since the inception of the Union Carbide Scholarship Fund in 1953, that liberal arts colleges and universities above and below the original size limitation of 500 to 1500 men have been selected. The decision to include some small colleges and large universities was made to give better balance to the program. With the new additions, 376 of a proposed goal of 400, Union Carbide Scholarships have been assigned to 45 educational institutions.

To give significance to the Union Carbide Scholarships offered by the large universities, which include California Institute of Technology, and Cornell, Duke, Princeton, Stanford, Notre Dame, and Pennsylvania Universities, the Boards of Admission of these universities have been asked to limit their selection to students showing a particular interest and exceptional ability in research.

As in the case of all Union Carbide Scholarships, the selection of the students and the administration of the scholarships is entirely in the hands of the participating colleges, technological institutes, and universities. Each scholarship covers the full four-year undergraduate tuition, plus an allowance, set by the college, for necessary books and fees. In addition, each scholarship carries an annual grant-in-aid of $500 for the college, plus a $100 allowance toward the expenses of a faculty advisor.

The purpose of the Union Carbide Scholarship program is to help make a college education financially possible for students who need or deserve such support and who are interested in future careers in business or industry; to help assure the availability of larger numbers of trained men and women for future executive and administrative careers in business and industry; and to encourage and give limited financial aid to a cross section of American colleges, technological institutes, and universities of traditionally high standing.

The 11 newly selected colleges and universities include: Cornell University, Duke University, Earlham College, Haverford College, Kenyon College, Princeton University, Randolph-Macon College, Southwestern at Memphis, Stanford University, University of Notre Dame, University of Pennsylvania.

A copy of the bulletin entitled "Union Carbide Scholarships" can be obtained by writing to The Union Carbide Educational Fund, 30 E. 42nd St., New York 17, N. Y.

EJC First General Assembly

Engineers Joint Council, constituted of eight major national engineering organizations with a total membership of 170,000, held on January 21 in New York its first General Assembly, a day-long program of presentations and discussions.

From every standpoint the conclave was an outstanding success—range of subjects, attendance, and participation. The attendance, approaching 400, represented not only the constituent organizations, but also several others of importance. Included were many of the nation's leaders in engineering, science, and industry. In the panels and forums the Government was represented by several spokesmen.

The spirit and hopes with which EJC had entered upon its first General Assembly were outlined by Thorndike Saville, Dean of Engineering, New York University, just elected to his second term as President of EJC.

The General Assembly served as an occasion for further announcement of details of the Nuclear Congress to be held, under EJC sponsorship and with the participation of other organizations, December 12–16, 1955, in Cleveland. The broad scope of this convention, momentous in its goals and magnitude, was related by Dr. John R. Dunning, General Chairman of the EJC Committee on Nuclear Engineering and Science, Dean of the School of Engineering, Columbia University, and by Dr. Donald L. Katz, Program Chairman for the Nuclear Congress, Chairman of the Department of Chemical and Metallurgical Engineering, University of Michigan.

Dow Forms New Dutch Subsidiary

The Netherlands Minister of Economic Affairs has granted The Dow Chemical Company permission to establish a wholly owned subsidiary company, to be known as Nederlandsche Dow Maatschappij N.V., in Rotterdam, Netherlands, Dr. Leland I. Doan, Dow president, has announced.

The Dow application to do business in The Netherlands, as approved by the Dutch government, permits the subsidiary to import, manufacture, and distribute domestically and abroad a variety of chemicals, plastics, and magnesium.

The new company plans to build a manufacturing plant as well as tank storage, warehouse, and dock facilities on a 50-acre tract leased for 20 years in the Third Petroleum Harbor at Rotterdam. The harbor is now being completed by the Port of Rotterdam, and construction on the plant site is expected to begin about mid-1955.

In addition to introducing basic chemical products to Dutch industry, Dr. Doan said the subsidiary will supply technical information for their use to help stimulate increased production of finished goods within The Netherlands economy for export and domestic sale. In this connection, he pointed out, a technical service and development group

will be attached to the Dutch concern to assist its industrial customers in their manufacturing operations.

Among the products the firm plans to process are Styron, Dow's widely known polystyrene plastic; magnesium alloys; glycols, including the versatile products known under the trademark of Dowanols; and certain other chemicals now undergoing economic study. Polystyrene production will include processing of Styron in a variety of colors for molded applications.

All sales for the Dutch company, both in The Netherlands and abroad, will be handled by two other wholly owned subsidiaries, Dow Chemical International Limited and Dow Chemical Inter-American Limited, with branch offices and sales representatives throughout the world.

Location of the new firm in Rotterdam will greatly speed up product delivery service, particularly in the European distribution area. It is expected products will be delivered from Rotterdam to European markets in three to six days.

Dow Chemical, pioneer in the transportation of bulk liquid and dry chemicals by water, will use leased tankers to carry basic raw materials from its U. S. plants to the Rotterdam plant. The subsidiary also will purchase Dutch and other European raw materials.

The firm will employ largely Dutch nationals, and certain qualified personnel will be sent to Dow plants in the United States for special training in production, technical service, and sales functions.

"Chicago Plan" for Engineering Societies

Reasons why the nation's major professional engineering societies should move their headquarters from New York City to Chicago are presented in a brochure being distributed to national officers of the organizations.

Economy, convenience of a centralized location, the availability of a choice Chicago site, and the services of the world's best-known technological library, are among the eight major reasons outlined in the booklet.

The brochure has been prepared by a committee of Chicago civic, educational, and industrial leaders because the societies must soon construct a new building to replace the present outmoded one at 33 W. 39th St., New York City, which has been their joint home during the past 50 years.

The situation has prompted society members in Chicago, Pittsburgh, Philadelphia, and Washington, D. C., to urge that the new headquarters be located in their respective cities. A decision by national officers of the groups on the future location was scheduled for early February.

Organizations for which the decision must be made include: American Society of Civil Engineers, American Society of Mechanical Engineers, American Institute of Electrical Engineers, American Institute of Mining and Metallurgical Engineers, and American Society of Chemical Engineers.

Savings of at least $2,470,000 in the cost of constructing the new headquarters building and $235,000 in annual operating expenses, plus a location that will grow in value through future years, will be attained by the societies in Chicago, the brochure contends.

The savings will be possible, it is pointed out, by the societies' use of the 5-acre city block (bounded by State, Dearborn, 31st, and 32nd streets in Chicago) offered them as a building site on the Technology Center campus of Illinois Institute of Technology, 15 minutes directly south of downtown Chicago. It is the only free land offered the organizations, in all the cities seeking the future headquarters, of sufficient size to permit construction of an economical two-story building that will contain a needed minimum of 250,000 square feet of floor space. The Chicago committee estimates that such a building will cost at least $1,000,000 less to build than a multistory structure containing equal area.

Further savings will be utilized at the Illinois Tech campus, the Chicago proposal points out, by the societies' use of the already available heating, parking, conference and meeting rooms, and eating facilities at Technology Center. This would spare construction, equipment, and later maintenance costs. Illinois Institute of Technology's 110-acre campus is the home of a number of affiliated scientific and engineering institutions, including the Armour Research Foundation, the Institute of Gas Technology, the Parmly Foundation for Auditory Research, the Institute of Psychological Services, and the Association of American Railroads Research laboratories. A housing and shopping area has been developed at the Center.

Another major factor in making the site economical, and the Chicago invitation attractive to the societies, the brochure reports, is the offer of The John Crerar Library to provide the library services which the societies are obligated to furnish their scattered members at an annual cost of more than $55,000. It is revealed in the brochure that the John Crerar board of directors are discussing a possible relocation of the library, now situated in Chicago's Loop, and at least its extensive technological collection, on the Illinois Tech campus.

The brochure points out that while the Illinois Tech site may offer the greatest combination of advantages there are five other special sites available in the Chicago area, including sites offered by the University of Chicago and Northwestern University.

It reports that gifts totalling $200,000 to help finance a Chicago-located headquarters have been pledged by a small number of Chicago companies and that there is certainty that these will be supplemented by others when it has been determined that the societies will locate in Chicago.

Co-chairmen of the Chicago committee which published the brochure are James D. Cunningham, chairman of Republic Flow Meters Company, and Dr. Robert E. Wilson, chairman of Standard Oil Company of Indiana. Other committee members are: Joseph L. Block, Henry Crown, Nelson C. Dezendorf, Willis Gale, Theodore V. Houser, Wayne Johnson, William V. Kahler, Lawrence A. Kimpton, Lenox Lohr, John L. McCaffrey, J. Roscoe Miller, James F. Oates, Jr., John T. Rettaliata, and H. P. Sedwick.

New Location for Olin Mathieson Sales Dept.

Headquarters for the Puritan Automotive Sales department of Olin Mathieson Chemical Corporation were moved on February 1 from Rochester to 10 Light St., Baltimore.

Manufacturing and research of the former Puritan Co., Inc., which merged with Olin Mathieson last year, will remain in Rochester.

W. Adrian King, director, Automotive Products, said integration of the Puritan sales staff with the other Automotive Products activity of the corporation will make it possible to provide improved service to jobbers and dealers by giving the Puritan sales group greater access to the corporation's staff services.

The Puritan line, sold through NAPA

jobbers, includes brake fluids, penetrant, flushing fluid, shock, jack, and knee action oil, and gasket seals.

J. E. Moore is sales manager, jobber accounts; B. A. Bannon, Jr., is assistant to the sales manager; and J. D. Ryan is field sales manager.

NSF Science Grants

The National Science Foundation, Washington, D. C., has announed 120 grants totaling about $1,600,000 for the support of basic research in the natural sciences, for conferences and studies on science, scientific information exchange, for the scientific manpower register, and for travel of American scientists to international scientific meetings.

This is the second group of awards to be made during fiscal year 1955 by the Foundation for the support of basic research and related matters. Since the beginning of the program in 1951, over 1200 such awards have been made, totaling about $12,750,000.

Grants announced recently were made to institutions and scientists in California, Connecticut, Georgia, Illinois, Indiana, Iowa, Kansas, Maine, Maryland, Massachusetts, Michigan, Minnesota, Missouri, New Hampshire, New Jersey, New York, North Carolina, Ohio, Oklahoma, Pennsylvania, Rhode Island, South Carolina, Tennessee, Texas, Utah, Washington, Wisconsin, and the District of Columbia. The research fields included are anthropology, astronomy, chemistry, developmental biology, earth sciences, engineering sciences, environmental biology, genetic biology, mathematical sciences, molecular biology, physics, psychobiology, regulatory biology, and systematic biology.

The research grants were approved by the National Science Board upon the recommendation of Dr. Alan T. Waterman, director of the Foundation.

PERSONALS

A. J. Kerbecek, Jr., is now project leader of the Westvaco Chlor-Alkali Division of the Food Machinery & Chemical Corp., South Charleston, W. Va. He was formerly research chemical engineer with the Atmospheric Nitrogen Fixation Group in the Ordnance Division at San Jose, Calif. This research group was completely disbanded, with personnel being transferred to other divisions of the Food Machinery Corp.

E. A. Tice, a member of the Corrosion Engineering Section of the Development and Research Division of The International Nickel Co., Inc.,

E. A. Tice

for the past eight years, has been transferred to the division's New England Technical Field Section at Hartford, Conn.

Robert T. Foley, specialist in materials and chemical process engineering, has joined the staff of General Electric Co.'s General Engineering Lab., Schenectady, N. Y. Dr. Foley, assigned as a corrosion engineer, was previously supervisor of general metallurgy in the G. E. Transformer Lab. at Pittsfield, Mass.

R. B. Mears, director of the Applied Research Lab. of U. S. Steel Corp., formerly in Pittsburgh, Pa., has been transferred to the company's new laboratory buildings located in Monroeville, Pa.

SAMUEL FORMAN WALTON

Samuel Forman Walton, vice-president and technical director of The Exolon Company, Tonawanda, N. Y., died on January 20, 1955, at the Buffalo General Hospital after an illness of about a month.

Mr. Walton was born on July 30, 1888 in Germantown, Pa. He spent his youth in Washington, Iowa, where he graduated from the local high school. After working for the Western Pacific Railroad for a short time, he entered Iowa State College and graduated with a B.S. degree in ceramic engineering in 1912. After several years in the refractory field, Mr. Walton joined the technical staff of The Carborundum Company in 1916. He joined Kalmus, Comstock & Wescott, industrial engineers, in Boston, Mass., in 1919, and from there went to Pennsylvania in 1923 to manage a clay plant. In 1925 he established a personal business as a refractory engineer in Philadelphia, but sold out in 1927 to become associated as a ceramic engineer with The Exolon Company. He later became technical director and in 1950 was elected a vice-president. He was responsible for much of the product development work which has been such an important factor in Exolon's growth. He has several patents to his credit in the field of abrasives and refractories, both in their production and in their use.

Mr. Walton was a Fellow of the American Ceramic Society and in 1942 received a professional engineering degree from the New York State College of Ceramics.

In addition to The Electrochemical Society, which he joined in 1949, Mr. Walton was a member of the American Chemical Society, the Institute of Ceramic Engineers, the New York State Ceramic Association, and the Abrasive Grain Association.

He is survived by his wife, the former Alice Osann; his son and daughter-in-law, Mr. and Mrs. Samuel Forman Walton, Jr., of E. Woodstock, Conn.; and two grandchildren, Stephanie D. and Cynthia L. Walton.

NEW MEMBERS

In February 1955 the following were approved for membership in The Electrochemical Society by the Membership Qualifications Committee:

Active Members

R. Porter Bailey, Quebec Metallurgical Industries Ltd., Box 340, Billings Bridge, Ottawa, Canada (Electrodeposition, Electrothermics & Metallurgy)

Philo Bailin, B. F. Goodrich, Sponge Products Div., Mail add: R.F.D. #2 Tashua Pky., Stepney, Conn. (Corrosion, Electrodeposition)

Walter W. Braun, National Lead Co., Titanium Alloy Mfg. Div., Niagara Falls, N. Y. (Theoretical Electrochemistry)

John E. Buskirk, Delco Battery Operations, Delco-Remy Div., General Motors Corp., W. Willard St., Muncie, Ind. (Battery)

WILLIAM CAMMACK, II, International Minerals & Chemical Corp., Mail add: 940 Ridge Rd., Lewiston, N. Y. (Industrial Electrolytic)

JEFFERSON CALVIN COLE, Diamond Alkali Co., Union Commerce Bldg., Cleveland 14, Ohio (Industrial Electrolytic)

RAYMOND T. DAVIS, JR., Applied Research Lab., United States Steel Corp., 234 Atwood St., Pittsburgh 13, Pa. (Theoretical Electrochemistry)

WILLIAM H. DEIERHOI, JR., National Carbon Co., P. O. Box 6087, Cleveland, Ohio (Battery, Electrodeposition)

ERNEST DOMOKOS, National Carbon Co., Mail add: 11409 Fidelity Ave., Cleveland 11, Ohio (Battery)

MICHAEL DOROTA, Tel-O-Tube Corp. of America, Mail add: 180 Van Riper Ave., East Paterson, N. J. (Electronics)

DAVID HART, Picatinny Arsenal, Mail add: 44 Parker St., Dover, N. J. (Corrosion)

CHARLES D'A. HUNT, Stauffer Chemical Co., Mail add: 24 Park Lane Dr., Orinda, Calif. (Theoretical Electrochemistry)

OLIVER C. JOHNSON, U. S. Metals Refining Co., Carteret, N. J. (Electrodeposition)

LESLIE H. JUEL, Great Lakes Carbon Corp., P. O. Box 637, Niagara Falls, N. Y. (Electrothermics and Metallurgy, Industrial Electrolytic)

FREDERICK A. KEIDEL, E. I. du Pont de Nemours & Co., Experimental Station, Wilmington, Del. (Theoretical Electrochemistry)

HENRI DE LACHEISSERIE, Société d'Electrochimie d'Ugine, 10, rue du Général Foy, B. P. 722-08, Paris, France (Industrial Electrolytic)

HENRY W. LAUB, Republic Steel Corp., Mail add: 768 E. 205 St., Euclid 19, Ohio (Electrodeposition, Electro-Organic, Industrial Electrolytic, Theoretical Electrochemistry)

ANDREW T. MCCORD, Carborundum Metals Co., Inc., P. O. Box 32, Akron, N. Y. (Electrodeposition)

DALE L. SCHECHTER, Dow Chemical Co., Mail add: 409 E. Haley St., Midland, Mich. (Industrial Electrolytic, Theoretical Electrochemistry

WILLIAM K. SIDWELL, Owens-Corning Fiberglas Corp., Mail add: 392 Hudson Ave., Newark, Ohio (Battery)

JAMES SOUTHWORTH, JR., National Carbon Co., U. C. C. Corp., Fremont, Ohio (Battery)

VANJA M. SREPEL, General Electric Co., Mail add: 240 Genesee Park Dr., Syracuse, N. Y. (Electronics)

JAMES C. STAMPS, Standard Electric Co., Inc., Mail add: 3016 Austin Hiway, San Antonio 9, Texas (Battery, Electronics, Theoretical Electrochemistry)

CHARLES D. STRICKER, American Steel and Wire Co., Mail add: 4281 Cricket Lane, Warrensville, Ohio (Corrosion, Electrodeposition, Industrial Electrolytic)

DAVID A. VERMILYEA, General Electric Co., Research Lab., Schnectady, N. Y. (Corrosion)

THEODORE N. YANNAKOPOULOS, National Bureau of Standards, Mail add: 6814 Westmoreland Ave., Takoma Park 12, Md. (Electrodeposition, Theoretical Electrochemistry)

Associate Members

YEICHI B. KATAYAMA, General Electric Co., Mail add: 716-20th South, Seattle 44, Wash. (Electrodeposition)

RICHARD M. PEEKEMA, General Electric Co., Mail add: 505 Basswood Ave., Richland, Wash. (Corrosion)

JOHN B. MAC CHESNEY, Oakite Products Inc., 19 Rector St., New York, N. Y. (Electrodeposition)

Student Associate Member

DONALD A. DUKELOW, Carnegie Institute of Technology, Mail add: Mounted Rt. 11, Ellwood City, Pa. (Electrothermics and Metallurgy)

Transfers to Active

HENRY B. MAIER, United Transformer Co., Mail add: 415 W. 118 St., New York 27, N. Y. (Electrodeposition, Electronics)

ALAN L. MCCLELLAND, Chemical Dept., Experimental Station, E. I. du Pont de Nemours & Co., Wilmington 99, Del.

JOSEPH G. SEVICK, St. Joseph Lead Co., Mail add: 126 Sawyer Dr., Crestmont, Aliquippa, Pa. (Electrothermics and Metallurgy)

Transfer to Associate

DEMETRIUS N. TRIADIS, Research Lab., International Nickel Co., Bayonne, N. J. (Corrosion, Electrodeposition)

New Sustaining Members as of January 1, 1955

BART MANUFACTURING COMPANY, Belleville, N. J. Representative: Dodd S. Carr

R.C.A. VICTOR DIVISION, Radio Corporation of America, Harrison, N. J. Representative: E. G. Widell

LETTERS TO THE EDITOR

Dear Sir:

I have read with great interest your editorial in the JOURNAL of The Electrochemical Society for November 1954 on "The Crisis in Science Teaching." This is one of the best articles on the subject I have seen published. It pleased all of us in Virginia that you mentioned the Virginia Junior Academy of Science and the work it is trying to do to stimulate student and teacher interest in science.

SIDNEY S. NEGUS
Medical College of Virginia
Richmond, Va.

"Contribution to the Theory of Electropolishing"

Dear Sir:

In his paper, Wagner[1] has carried out an interesting mathematical analysis of the smoothing that occurs during electropolishing. Since his analysis is based on the "acceptor" theory of polishing, we wish to point out that similar results can be obtained without making any assumptions about the mechanism of the polishing process.

In order to do this, it is only necessary to assume that the rate of metal removal is determined by the local curvature of the surface. The basis for this assumption is the work carried out by Edwards[2] and Hickling and Higgins[3] using composite anodes consisting of thin metal sheets clamped together and insulated from each other. By connecting alternate sheets in parallel and arranging for one set to extend further into the solution than the other, it was possible to study the current distribution for an anode of alternate peaks and valleys. The results showed that the current density at the peaks was higher than the current density in the valleys and that the ratio of peak current density to valley current density increased with increasing difference in level between the sets. Thus, to a first approximation, it seems reasonable to postulate that the current density at any point (and hence the rate of metal

[1] CARL WAGNER, *This Journal*, **101**, 225 (1954).

[2] J. EDWARDS, *ibid.*, **100**, 223C (1953).

[3] A. HICKLING AND J. K. HIGGINS, *Trans. Inst. Met. Finishing*, **29**, Advance Copy No. 10 (1953).

removal) exceeds the mean current density (mean rate of metal removal) by an amount proportional to the curvature of the surface at that point. Therefore, provided that the surface is not too rough, we can write

$$-\frac{\partial S}{\partial t} = C - \alpha \frac{\partial^2 S}{\partial x^2} \qquad \text{(I)}$$

where α is a positive constant having the dimensions of a diffusion coefficient and the other symbols are as defined by Wagner. Such an equation was originally suggested by Bertein,[4] although the underlying assumption was not clearly stated.

Subject to the conditions:

$$S = S_1 + b_0 \sin (2\pi x/a) \text{ for } t = 0$$

and

$$S \text{ finite for } x \longrightarrow \pm\infty$$

the solution of equation (I) is

$$S = S_1 - Ct + b_0 \cdot \sin (2\pi x/a) \exp (-4\pi^2 \alpha t/a^2). \qquad \text{(II)}$$

This solution is identical with the solution of Wagner's equations (VIII) and (XIII), provided we identify with $au/2\pi t = aC/2\pi$. Both theories therefore predict that, by plotting $\ln(b_0/b)$ against $\Delta m/A$, a straight line should be obtained. However, Wagner predicts that the slope of this line should be $2\pi/\rho a$, both ρ and a being measurable quantities, whereas our analysis suggests that the slope should be $4\pi^2\alpha/\rho C a^2$ where ρ, C, and a are measurable, but α is an unknown constant.

The only experimental data available for testing these expressions is that given by Edwards[5] for the smoothing of copper in orthophosphoric acid. Using his results to plot $\ln(b_0/b)$ against $\Delta m/A$, a reasonably straight line is obtained (Fig. 1). Moreover, as Wagner has pointed out, the slope of this line is in agreement with his expression. However, it is also in agreement with ours if $\alpha = 10^{-9}$ cm²/sec (C is assumed to be 10^{-4} cm/min).[6] Thus, although this work does not distinguish between the two theories, it is clear that extra experimental work on similar lines should be able to do so. For example, if experiments were carried out on specimens having corrugations of wave length $\frac{1}{2}a$, the slope of the $\ln(b_0/b)$ vs. $\Delta m/A$ line should be doubled on Wagner's theory, but quadrupled on ours. It would be most interesting if such work were carried out as it could provide a quantitative test of the "acceptor" hypothesis.

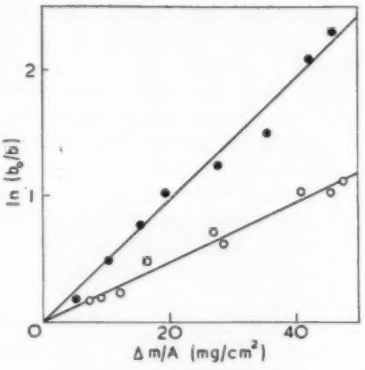

FIG. 1. Plots of $\ln(b_0/b)$ against $\Delta m/A$ for electrolytic (●) and chemical (○) polishing of copper. The figures have been calculated from the results of Edwards.[5]

It is clear that our analysis can be applied to any process involving a rate of metal removal dependent on the geometry of the surface profile. Such conditions apparently exist in etching and chemical polishing in addition to electropolishing. For example, Edwards, using the laminated anode technique for copper in orthophosphoric acid, has shown that the ratio of peak current density to valley current density does not change markedly on passing from etching to polishing conditions. Further, Marshall[7] has noted that, during the chemical polishing of iron in an oxalic acid/hydrogen peroxide/sulfuric acid solution, the relatively coarse textures are only partially removed, while the fine "secondary" textures superimposed upon the main textures are completely removed. Such behavior is predicted from our theory, for, provided the initial surface profile is periodic, it can be represented by a Fourier series with coefficients, b_n, and the final profile is then given by

$$S = S_1 - Ct + \frac{\infty}{Z_1} b_n \sin (2\pi n x/a) \exp (-4\pi^2 \alpha n^2 t/a^2). \qquad \text{(III)}$$

Thus, during treatment the higher harmonics should disappear more rapidly than the fundamental, and the surface profile should tend to become sinusoidal.

The only data available for testing the theory in the case of chemical polishing is that of Edwards for copper in a well-stirred orthophosphoric acid/acetic acid/nitric acid mixture. As shown in Fig. 1, $\ln(b_0/b)$ is again a roughly linear function of $\Delta m/A$. Assuming $C = 10^{-2}$ cm/min,[8] equation (II) implies $\alpha = 10^{-6}$ cm²/sec. In this case, it would be unfair to apply Wagner's theory since his treatment does not take account of the liquid flow that occurs at the metal surface in a stirred bath. On the other hand, our theory appears to describe the smoothing reasonably well, but more experiments are necessary before any significance can be given to the constant α.

J. F. NICHOLAS AND W. J. MCG. TEGART
Division of Tribophysics
C.S.I.R.O.
Melbourne, Australia

BOOK REVIEWS

ELECTROMETRIC *p*H DETERMINATIONS by Roger G. Bates. Published by John Wiley & Sons, Inc., New York, 1954. 331 pages, $7.50.

This is a fine book. However, before describing its virtues one should express a word of caution. For every freshman knows what *p*H is—it's the logarithm of the hydrogen ion concentration, I mean the negative log. Moreover, every technician knows how to measure it—with a *p*H meter, what else? Such audiences as these will surely wonder why a simple topic like this requires 328 pages of treatment when, after all, the logarithm tables are so much more precise and the Beckman's, L & N's, etc., sit bright and shiny on the laboratory bench.

This word of caution should not, of course, be used to discourage the research worker or serious student interested in the real meaning of his or other measurements of acidity. The problems in such measurement are *not* simple; neither, incidentally, are they as complex as in the past they have been made to seem. The unified and comprehensive treatment presented in this book makes clear just where the pitfalls are and what can be done to avoid or minimize them.

The book is divided about equally between the experimental and theoreti-

[4] F. BERTEIN, *Compt. rend.*, **220**, 684 (1945).

[5] J. EDWARDS, *This Journal*, **100**, 189C (1953).

[6] P. A. JACQUET, *Métaux, corrosion, usure*, **18**, 1 (1943).

[7] W. A. MARSHALL, *Research*, **7**, 89 (1954).

[8] R. PINNER, *Electroplating and Metal Finishing*, **6**, 360 (1953).

cal aspects of acidimetry. The various definitions of *p*H are described in systematic fashion, the liquid junction potential problem is nicely treated, and a particularly good treatment of nonaqueous solutions is presented. The experimental sections include detailed instruction in the preparation of cells, electrodes, and controls. The book reads easily throughout, and the format and typography are good.

J. F. DEWALD

FERRO LEGIERUNGEN, German translation from the Russian, by W. P. Eljutin, J. A. Pawlow, and B. E. Lewin. Published by VEB Verlag Technik, Berlin, 1953. 440 pages, price 25 West Marks.

Any new book on the metallurgy of ferroalloys excites some curiosity because of the severe want of informative literature on this subject, especially in this country, as has been stressed in our review of the similar book by Durrer-Volkert in the June 1954 issue of the JOURNAL (page 158C). To know what is happening behind the Iron Curtain in this field so intimately connected with armament may be another incentive for examining the monograph cited in the title. The first of the authors has a reputation as an electrometallurgist in his own country as appears from various of his publications. This ought to give his writing some level.

We of the capitalistic world are not prejudiced in any way against famed Russian metallurgists whose illustrious names have, in past times, marked in great numbers the road of progress in metallurgy. It seems, however, that Russian authors, like those of this book, always have to fight some inferiority complex which induces them to deceive their own people as to the originators of inventions. This makes them rather amusing to us. In the present case, for instance, the preface, which in Russian books always carries the bulk of political propaganda, tells us that Petrow is the father of the electric arc furnace since he reduced the oxides of mercury, tin, and lead in an arc struck between two carbon pencils, with the current of a large battery. Beketow is next called the creator of the aluminothermic process for having reduced barium oxide with aluminum. That is definitely a lie, since Woehler, who in Germany made the first aluminum by sodium reduction of the chloride, used this metal three years earlier than Beketow for the reduction of iron oxide. Another technique of indoctrination, Russian style, is to ignore names. Eljutin, *et al.*, are hit with amnesia as to the name of H. Goldschmidt and as to his connection with aluminothermic methods. Nor do they mention anywhere Soederberg or Girod, while Moissan and Heroult are given some faint recognition. This generosity is dimmed by the fact that the bibliography contains only five foreign references out of a total of 101. Pictures are given of Beketow, a bearded gentleman who lived in tsarist times and who, therefore, smiles broadly, as well as those of four comrades who had the bad luck of spending their life under communist rule and look very sad indeed, as though they just escaped a purge or a brain washing of some sort. Uncle Stalin is, of course, extolled in the preface as the great man who brought about the development of the Russian ferroalloy industry, and his merits are stressed repetitiously in the introduction to a number of chapters. The foreign capitalists of tsarist times are accused of having refused to tell the Russians how to prepare ferroalloys in contradiction with some assertions of the authors who claim that the ferroalloy processes are the invention of Russians. Naturally the fact that Siemens & Halske built for Russia in the thirties the biggest ferromanganese plant in the world at the Dnieper, and put it in operation, is nowhere even mentioned.

This book is said to be written for advanced students of metallurgy and for engineers in general, who want to devote themselves to the production of ferroalloys. This gives it its general character, and the didactic side is well enough taken care of. Each chapter on the alloys is provided with a section on physical chemistry, thermodynamics, constitution diagrams of alloys and slags, heat balances, and calculations of burdens. Since all references as to the origin of the data used are left out, it is impossible to check the value of the calculations based on them. Alloy and slag diagrams seem to have been taken mostly from M. Hansen's handbook and from Gmelin, which gives them the 1935–1936 vintage. The unreliability of the information offered may be seen from the citation that a manganese 99.999 can be made by calcium reduction, chromium 99.96 by hydrogen reduction of oxide.

The individual chapters concern the following subjects: thermodynamics in general, ferrosilicon, silicoaluminum, silicocalcium, ferromanganese, ferrochrome, ferrotungsten, ferromolybdenum, ferrovanadium, ferrotitanium, zirconium alloys, ferroniobium, ferroboron, ferrophosphorous, electro pig-iron, furnace construction and operation, plant layout, economics.

All appearances are that much of the material offered is extracted from operations in seized German Sachsony and Silesia ferroalloy plants and from their kidnapped metallurgists. The chapter on vanadium from slags, for instance, which may be compared with the one in Durrer-Volkert's book, describes essentially the German technique. The one on ferrochrome does not reveal anything beyond the principles of silicothermie. Those on the production of aluminothermic ferrotitanium and on ferrosilicozirconium are acceptable. The construction of a combined bessemer/arc furnace is of interest and the equipment drawn up might fit many research projects. The most grievous omissions concern a treatise of refractories, electrode materials, construction of furnaces, their regulation, and the whole electrical arrangements. These subjects are sketched very vaguely on 12 pages as against 190 pages in the book by Durrer-Volkert.

In general it may be said that if the monograph by Eljutin, *et al.*, represents truly the present status of the Russian ferroalloy industry, Ivan will still have a lot to plagiarize from the capitalistic world just to get in line. Name stealing alone will not do it.

W. J. KROLL

LITERATURE FROM INDUSTRY

CHLOROTHENE. Information on Chlorothene (Dow Inhibited 1,1,1-Trichloroethane), a new cold degreasing solvent has been compiled in a pamphlet which is now available. The pamphlet covers specifications, properties, relative evaporation rates, toxicity factors, and vapor pressure. Chlorothene's low toxicity, high solvent power, and stability recommend it for cold-cleaning, dip-cleaning, and bucket-cleaning operations. The Dow Chemical Co. P-283

WARREN SPECTRACORD. New 20-page booklet gives the whole story of the Warren Spectracord, announced as the fastest recording - spectrophotometer commercially available. Three pages are devoted to circuit diagrams and step-by-step explanations of the instrument's unique electronic recording and control systems. Included are actual-size fac-

similes of absorption spectra run on the Spectracord (benzene vapor in 4½ min, chloroform in 2½ min, didymium glass in 45 sec) to demonstrate its high resolution, speed, and reproducibility. Fisher Scientific Co. P-284

COLLOIDAL GRAPHITE. Revised 4-page bulletin containing photographs, diagrams, charts, and information on the advantages offered by colloidal graphite in the assembly and run-in of machines has been released. The bulletin shows how to use colloidal graphite, chiefly in the form of a petroleum oil dispersion. 'dag' Colloidal Graphite gives smoother bearing surfaces, increased power from reduced friction, lower bearing temperatures, reduced oil consumption, shorter run-in periods, protection against temporary failure of oil supply or rupture of oil film, less corrosion of cylinder walls and piston rings, fewer replacements, lower maintenance costs for bearings and friction surfaces, and longer useful operating life of engines and other machinery. Acheson Colloids Co. P-285

INTRODUCTION TO ELECTRODEPOSITION. Just off the press is a bulletin entitled "Apparatus for Analysis by Electrodeposition." It shows, in 12 fully illustrated pages, why laboratory analysis via electrodeposition of elements is accurate, specific, time-saving, and convenient. The various forms are defined (gravimetric, polarographic, amperometric). Fisher instruments for the methods are discussed in detail: Electro-Analyzer, Elecdropode, Amperometric Titrimeter, T.E.L.-Meter. Available without charge. Fisher Scientific Co. P-286

PRESSURE TRANSDUCER. New brochure describes the "Dual Element Pressure Transducer" that translates static and dynamic air pressures to equivalent voltages. Lists altitude and velocity computations, among a wide range of applications for the potentiometer type pressure transducer. Copy upon request. Technology Instrument Corp. P-287

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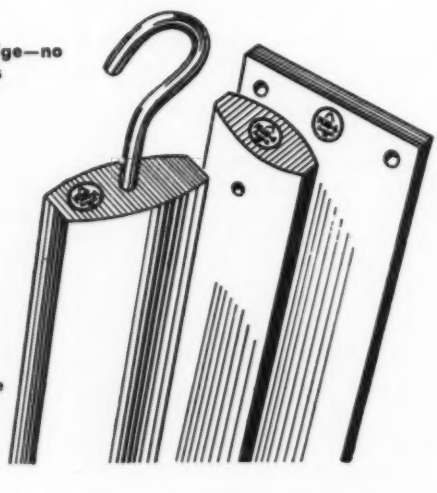

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A Further Study of Electrodeposited Manganese Dioxide Electrodes[1]

W. C. Vosburgh, Richard S. Johnson, John S. Reiser, and Douglas R. Allenson

Duke University Durham North Carolina

ABSTRACT

Manganese dioxide electrodes prepared by electrodeposition on graphite rods were discharged in ammonium chloride electrolyte of *p*H 7.2 to 7.5. Two discharge products were identified and measured, an oxide with a composition of about $MnO_{1.6}$, and manganese (II) ion which appeared in the solution. The electrical output was accounted for satisfactorily by these two products. Atmospheric oxygen had only a small effect on the discharge.

Electrodes of the same type decreased slowly in potential on standing in ammonium salt electrolyte. The decrease continued for many months and its rate was independent of the anion present and of the presence or absence of oxygen. Similar electrodes on platinum instead of carbon decreased appreciably faster. Analyses and discharges of electrodes that had stood in electrolyte showed a loss of available oxygen.

Introduction

Some aspects of the behavior of manganese dioxide electrodes prepared by electrodeposition on graphite rods were left unexplained in the work of Ferrell and Vosburgh (1). Such electrodes in ammonium chloride electrolyte of *p*H 7 were not very reproducible and decreased in potential with time on open circuit. Discharge sometimes gave a capacity more than that calculated on the basis of reduction to the oxyhydroxide, MnOOH. It was suggested that reduction below the trivalent state might have taken place. However, reaction of oxygen from air, which was not excluded, would also give an apparent excess capacity. This reaction has been considered to play a part in the discharge of manganese dioxide electrodes (2–4).

It has been found that the excess discharge capacity is mainly the result of reduction of part of the dioxide to manganese (II) ion in agreement with Cahoon (5). The reaction of atmospheric oxygen was relatively unimportant. The decrease in open-circuit potential is at least partly the result of a slow decrease in available oxygen on long standing in ammonium salt electrolyte.

Experimental

Preparation, Measurement, and Discharge of Electrodes

Most of the manganese dioxide electrodes were prepared as described by Ferrell and Vosburgh (1). Briefly, graphite rods of highest purity were sealed in glass tubes so that 8 cm^2 of surface was exposed. Manganese dioxide was deposited electrolytically on this surface from an acid manganese (II) sulfate bath at about 80°C by means of a current of 25 ma (3.1 ma/cm^2) for either 15 or 30 min. The longer time is to be assumed unless otherwise indicated.

Treatment of the graphite rods before they were plated was found to be of some importance. The usual treatment was to immerse the rod in water while the water was boiled and then cooled. This seemed to give more uniform results than did no treatment.

Two other treatments were used. In what will be called the oxygen treatment, the rod was made the anode in the electrolysis of dilute sulfuric acid. In the hydrogen treatment, the rod was made the cathode in a similar electrolysis.

It was found necessary to wash the manganese dioxide electrodes thoroughly as the final step in their preparation. They were allowed to stand in frequently changed distilled water until no more acid was washed out and then kept in distilled water until used. If not thoroughly washed, manganese (II) ion from the plating bath was retained as well as acid.

When open-circuit electrode potentials only were to be measured, four or more electrodes were mounted in a rubber stopper fitting a vessel of about 200 ml capacity. In the vessel was placed about 180 ml of electrolyte, or enough to cover the manganese dioxide. A hole in the stopper allowed insertion of a bridge to a reference electrode, which was either a saturated calomel electrode or a silver chloride electrode which had been checked against a calomel electrode. The electrode potentials are given as measured against the calomel electrode.

The electrolyte was 2M NH_4Cl with enough

[1] Manuscript received May 3, 1954. This paper was prepared for delivery before the Boston Meeting, October 3 to 7, 1954.

ammonia added to bring the *p*H to 7.2 to 7.5, except as otherwise noted. The *p*H was measured by means of a glass electrode and Beckman *p*H meter.

When electrodes were to be discharged they were transferred singly to a vessel holding about 250 ml of the electrolyte. A large cylindrical silver electrode was used as the anode. The electrode to be discharged was mounted in the center of the vessel and centrally with respect to the anode by means of a rubber stopper, which also bore a reference electrode and gas-inlet and outlet tubes. Either air or nitrogen was passed through the solution continuously during the discharge. Current from three dry cells in series was passed through a variable resistance, a calibrated milliameter, and the cell composed of the experimental manganese dioxide electrode and the silver anode. The initial current was adjusted to 0.1 ma/cm^2 and fell to about 0.09 ma/cm^2 at the end of the discharge. The current and the potential difference between the manganese dioxide electrode and reference saturated calomel electrode were measured frequently. The discharge capacity was taken as the summation of current in milliamperes times time in minutes to the time when the potential difference had fallen to zero from an initial value of 350 to 450 millivolts. The fall in potential from about 100 mv to zero was rapid, indicating approximate completion of the discharge.

All measurements were made at room temperature, which was never far from 25°C. The change of electrode potential with temperature in the vicinity of 25°C was found to be −0.0006 v/degree, and temperature errors were seldom more than a millivolt.

Analytical Methods

A number of electrodes were analyzed either as prepared, or after standing in electrolyte, or after discharge. Without weighing, one or more electrodes were digested on a steam bath with a measured volume of 0.025 or 0.1*N* arsenious acid solution to which some sulfuric acid had been added. When the oxide was dissolved and the graphite rod thoroughly washed, the excess arsenious acid was titrated with permanganate. The total manganese was then determined in the same solution after addition of pyrophosphate by potentiometric titration with permanganate (6). This method proved to be defective when applied to electrolytic manganese dioxide on graphite rods, though it has given good results for precipitated manganese dioxide. However, even for the electrolytic oxide it gives fairly reproducible results under a given set of conditions and, because of this, some useful information can be gained from the analytical data.

TABLE I. *Analytical results for some representative electrodes*

No. of electrodes	Reducing solution	Mn, total per electrode m-moles	O available per electrode m-moles	x in MnO_x
2[a]	0.1*N* H_3AsO_3	0.223[a]	0.201[a]	1.90
1[a]	0.1*N* H_3AsO_3	0.220[a]	0.180[a]	1.82
1[b]	0.1*N* H_3AsO_3	0.216	0.186	1.86
6	0.025*N* H_3AsO_3	0.209	0.137	1.65
2[c]	0.025*N* H_3AsO_3	0.213	0.114	1.53
4	0.02*N* $FeSO_4$	0.212	0.185	1.88
1	0.02*N* $FeSO_4$	0.172	0.142	1.83

[a] Each sample consisted of four 15-min electrodes each. The manganese and available oxygen were calculated on the basis of a two-electrode sample.

[b] Two 30-min electrodes analyzed as one sample.

[c] These electrodes were placed in 1M ammonia solution for an hour before analysis.

Some typical results on freshly prepared electrodes are given in Table I. For the data in the first three rows, the standard solution for the available oxygen determination was 0.1*N* arsenious acid while, for the data in the fourth and fifth rows, the solution was 0.025*N*. This apparently minor change in procedure led to a large decrease in the apparent x-value in the formula MnO_x. This suggests that the x-value 1.90 may be too small. The data in the last two rows of the table were obtained with a 0.020*N* iron (II) ammonium sulfate solution substituted for the arsenious acid solution. In this case it was necessary to protect from oxygen while dissolving the manganese dioxide as well as during the final titration. The iron method agrees fairly well with the 0.1*N* arsenious acid method.

Comparison of the fourth and fifth rows shows another source of error in the arsenite method. Manganese dioxide adsorbs ammonia or ammonium ion, and electrodes treated with an ammonia solution can be expected to retain some ammonia (7). Such electrodes give lower x-values than untreated ones, the retained ammonia apparently affecting the results.

The reproducibility of the electrodes was shown by the analytical data. There is probably little error in the total manganese determination. Of 13 electrodes similarly prepared, two were abnormally low in total manganese, one of them being the single electrode in the last line. If these two are excluded, the average total manganese was 0.213 millimole with a standard deviation of 0.006 millimole, or 3%. The average apparent x-value for the group of six electrodes, 1.65, had a standard deviation of 0.05.

Discharge Experiments

Discharges were made in air and nitrogen atmospheres for checking the effect of oxidation by air. Provision was made for examination of the reduction products. Cahoon (5) found that reduction in the

presence of a large volume of electrolyte gave only manganese (II) ion. At the much higher *p*H of the present investigation this product is less probable, judging from equilibrium measurements of McMurdie, Craig, and Vinal (8), but it was found in considerable quantity in the electrolyte after discharge. The quantity was determined by potentiometric titration with permanganate in the presence of pyrophosphate (9). The manganese oxide remaining on the electrode after discharge to zero potential against the saturated calomel electrode was analyzed for available oxygen and total manganese with the use of 0.025*N* arsenious acid solution. Data for eight discharges are given in Table II.

The first four electrodes were given the oxygen treatment prior to electrodeposition of the manganese dioxide, and the other four the boiling treatment. The only difference in these experiments that can be ascribed to the treatment of the graphite is that the total manganese (sum of columns 3 and 4) in the oxygen group was 6% less on the average than that of the others. A similar difference was noticed in the total manganese of the two kinds of electrodes when they were analyzed undischarged. For 15-min electrodes with a more severe oxygen treatment the difference was larger, 0.112 millimoles of manganese for normal electrodes and 0.081 millimoles for oxygen-treated.

The electrical outputs varied rather widely. The amount of manganese (II) ion in solution was fairly uniform and was almost half of the total manganese. The oxide remaining on the electrode after discharge to a potential of zero against the saturated calomel electrode varied from $MnO_{1.48}$ to $MnO_{1.58}$. It made little difference whether a current of air or a current of nitrogen was passed through the solution before and during discharge. As indicated in the sixth column, half of the discharges were made one way and half the other. In the last column are given the ratios of oxygen to manganese in the original oxides as calculated from the discharge data. These values are much less variable than any of the other data and are appreciably higher than the original electrode compositions as found by analysis. They are based on the assumption that part of the original oxide was reduced to the oxide remaining on the electrode after discharge and the remainder to the manganese (II) ion found in solution. The calculated original oxide of the four air discharges is somewhat richer in oxygen than that of the nitrogen discharges. This indicates a small oxidizing effect of atmospheric oxygen during the discharge. Another minor effect of the atmospheric oxygen may be on the amount of manganese (II) ion formed, which was in all cases smaller in the air discharges than in the nitrogen discharges.

TABLE II. *Discharge data*

Electrode No.	Output ma-min	Mn^{++} in solution m-moles	Mn on electrode m-moles	O available, electrode m-moles	Gas present	Original oxide x in MnO_x
25	336	0.079	0.095	0.055	air	1.92
26	367	0.086	0.100	0.054	N_2	1.91
28	352	0.077	0.107	0.061	air	1.92
29	354	0.082	0.083	0.040	N_2	1.91
47	386	0.081	0.105	0.051	N_2	1.92
48	426	0.077	0.121	0.059	air	1.97
49	404	0.081	0.115	0.060	N_2	1.93
50	378	0.075	0.097	0.051	air	1.98

There were two sources of error in the data from which the original compositions in the last column of Table II were calculated. One was the separation of a small amount of oxide from the electrode during discharge. The total manganese found on the electrodes and in solution after discharge was one to two milligrams less per electrode than the total manganese on undischarged electrodes according to Table I. The separated oxide could be observed, but was small enough to escape detection unless sought. If this oxide were lower oxide, the x-values would be too high; if it were dioxide, there would be little error. The other source of error was in the available oxygen determination, for which the method was questionable, and would lead to low x-values. The two errors might compensate or the second might predominate. It seems probable that the average x-value for the discharges in nitrogen, 1.92, represents a minimum for the original oxide in spite of the lower analytical values for undischarged electrodes as shown in Table I.

To check the hypothesis that the composition given above for the discharged electrodes is too low, additional electrodes were discharged and analyzed. Five electrodes analyzed using 0.1*N* iron (II) sulfate as the reducing agent gave an average x-value of 1.58 with a range from 1.55 to 1.61. The eight electrodes of Table II averaged 1.53 with a range from 1.48 to 1.58. The difference is not large in view of the variation of the electrodes, but is in the expected direction, since the iron sulfate method gave more nearly correct results than the dilute arsenious acid method for freshly prepared electrodes.

In addition, the oxide was scraped from four discharged electrodes and analyzed without the presence of the graphite rod. The electrodes were discharged with a current density of 0.4 ma/cm^2, and it is possible that, because of the high current density, the oxide might be a little too high in available oxygen, although there is no evidence for this at present. By 0.025M iron sulfate two samples gave 1.61 and 1.61, and by 0.025 arsenious acid two others 1.62 and 1.63 for x. Both methods give correct results for precipitated manganese dioxide. Therefore, it is

probable that the values for available oxygen in Table II are somewhat too low, and that the oxide resulting from the discharge of manganese dioxide under the conditions of the present work is richer in available oxygen than $MnO_{1.5}$. Feitknecht and Marti (10) showed that the ratio of oxygen to manganese in manganese oxyhydroxide can vary.

Change in Electrode Potential on Standing in Electrolyte

The results of most of the experiments on the change in electrode potential on standing in electrolyte are given in Fig. 1. All of the electrodes were prepared by electrodeposition for 15 min. Each point on or near curves B and C represents the average potential of four electrodes in the same solution. The points on curve A represent the average of three such groups.

The region between the two dashed curves represents seven different groups of four electrodes each, all of which decreased in potential at about the same rate. Curve B is drawn through the average values for three closely agreeing groups, but the points are omitted to avoid confusion; the points shown on curve B belong to a fourth group.

The three groups of curve B had air, oxygen, and nitrogen atmospheres, respectively, with the electrolytes saturated with these gases. No significant differences could be detected. This was true also of the three groups represented by curve A in which the manganese dioxide was deposited on platinum instead of graphite, and in which the electrolytes were saturated with air, oxygen, and nitrogen. The electrodes on platinum decreased at a greater rate than similar electrodes on carbon.

There are three sets of points between the dashed lines representative of electrodes in 2M ammonium bromide, 2M ammonium fluoride, and 1M ammonium perchlorate with enough ammonia in each case to give an initial *p*H of from 7.2 to 7.5. Finally, one group is included for ammonium chloride and the hydrogen treatment of the graphite prior to the electrodeposition of the manganese dioxide. The changes on standing are independent of the anion present.

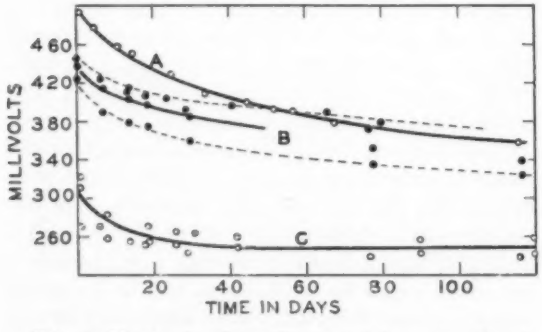

FIG. 1. Change in electrode potential on standing in ammonium salt electrolyte. Curve A represents electrodes of manganese dioxide on platinum, curve B and the region between dotted lines, electrodes on graphite, and curve C, electrodes on oxygen-treated graphite.

Changes in electrolyte *p*H, measured after the period of observation, up to 0.25 units had occurred, some in one direction and some in the other. Correction for these would not alter the conclusions, and were not made.

Different groups of electrodes had somewhat different initial potentials, and the differences were maintained for the most part throughout the period of observation; the changes were more consistent than the electrode potentials. The decrease in electrode potential with time is characteristic of all groups represented by curves A and B. For some of the groups it continued for 100 days beyond the period shown in Fig. 1.

The three groups of electrodes represented by curve C were those in which the electrodeposition had followed an oxygen treatment of the graphite. The potentials were much lower than those of the other groups and nearly constant, after an initial decrease. They averaged 0.25 v at *p*H 7.5 after more than 200 days, with changes of only a few millivolts after the first month.

That the oxygen treatment gives lower electrode potentials than the normal treatment has been verified in later experiments. The effect varies inversely with the thickness of the oxide layer. For 30-min electrodes no difference is noticed at first but, on standing in electrolyte, the oxygen-treated electrodes decrease faster in potential than the others, falling to a lower value in a short time.

The decrease in electrode potential might have been the result of ion exchange with the electrolyte (7), or of slow loss of available oxygen (11), or it might have been a change from a less stable to a more stable crystal form, or a combination of the

TABLE III. *Discharge data for electrodes that had stood in electrolyte more than two years*

Electrode No.	Storage electrolyte	Output ma-min	Mn^{++} in solution m-moles	Mn on electrode m-moles	O available, electrode m-moles	Original oxide x in MnO_x
79	NH_4Cl	149	0.0501	0.0330	0.0192	1.79
80	NH_4Cl	104	0.0328	0.0245	0.0154	1.84
81	NH_4Cl	115	0.0376	0.0387	0.0183	1.71
82	NH_4Cl	120	0.0427	0.0327	0.0200	1.76
59	NH_4Br	186	0.0641	0.0533	0.0332	1.78
60	NH_4Br	165	0.0398	0.0632	0.0442	1.92
62	NH_4F	176	0.0602	0.0498	0.0286	1.76
63	NH_4F	199	0.0696	0.0440	0.0267	1.78
73	NH_4ClO_4	146	0.0359	0.0243	0.0186	2.06
74	NH_4ClO_4	156	0.0574	0.0325	0.0208	1.77

three. Analyses indicating a loss of available oxygen were found later to be untrustworthy because of the interference of ammonium ion as illustrated in Table I and confirmed by later experience.

Some of the electrodes not used for analysis were observed for a period of over two years. The potentials continued to decrease and at the end of this time were 0.28, 0.27, and 0.25 v (corrected to *p*H 7.5) for three groups made with ammonium bromide, ammonium fluoride, and ammonium perchlorate electrolytes, respectively. A fourth group, not previously described, of 12 electrodes in chloride electrolyte fell to 0.25 v during this time. Electrodes from each of these four groups were discharged to determine their composition after the long standing in electrolyte. Discharges were made as described above, with analysis of the products and calculation of the composition before discharge as for the experiments of Table II. In the analyses of the discharged electrodes 0.025*N* iron (II) sulfate was used for the available oxygen determination except that 0.025*N* arsenious acid was used for electrodes 79, 80, and 82. Results are shown in Table III.

All discharges made are reported in Table III. The one leading to an original x-value of 2.06 must have been in error, although no source of error was recognized. In most cases, the calculated original ratio of oxygen to manganese (in terms of x in MnO_x) is so much less than the similar values given in Table II for fresh electrodes that it must be concluded that some of the available oxygen has been lost.

The decrease in electrode potential on standing can be explained as the result of the loss of available oxygen. A rough estimate of the capacity loss on standing can be made from the change in electrode potential, with the help of an appropriate open-circuit discharge curve (1). The loss estimated in this way is in as good agreement as could be expected with that estimated from the data of Table III.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 Journal.

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The Anodic Treatment of Aluminum in Sulfuric Acid Solutions[1]

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ABSTRACT

High purity aluminum was anodized in sulfuric acid solutions at various concentrations (5 – 50%), temperatures (10° – 50°C), time periods (2 – 60 min), and current densities (1.7 – 6.2 amp/dm²). The coating weight, metal loss, coating ratio, sealing weight gain, dyed color, density, and coating chemical dissolution rate were determined.

Introduction

The sulfuric acid anodizing process for aluminum and its alloys has been adopted widely in industry. By this technique the thickness of the natural oxide film on aluminum can be greatly increased, thus either strengthening many of the oxide film's inherent properties, such as its high corrosion resistance, or contributing new characteristics, such as the ability to become colored by organic dye adsorption.

Early quantitative studies (1) of anodic processes dealt with the metal dissolution and coating formation and determined the current efficiency with respect to these two processes. Later, Anderson (2) presented a theoretical analysis of the mechanism of anodic coating formation. He employed the term "efficiency ratio," defined as the coating weight per gram of metal consumed with a maximum value of 1.89. Anderson's theory indicated that, in sulfuric acid type electrolytes, the highest efficiency ratio would be considerably below this value since part of the aluminum dissolved by anodic reaction diffuses into the electrolyte without forming oxide.

Mason and Slunder (3) presented the results of a broad and detailed quantitative study of the anodic reactions of aluminum in sulfuric acid solutions and their variation with anodizing time, alloy composition, electrolyte concentration, and temperature, etc. The effect of these variables on the efficiency ratio, now termed "coating ratio," was discussed. A similar but less extensive paper was published later by Chanda (4). Kronsbein (5), and Bradshaw and Clarke (6) have continued this study. Their evaluation of the extent of other anodic reactions is of special interest. A recent paper by Mason and Fowle (7) discussed the variation of coating ratio during anodizing under various current densities and at temperatures between 1° and 21°C.

The present investigation employed sulfuric acid solutions and used the technique of Mason and Slunder but extended the range of the several variables studied, noting their effect, not only on metal loss, coating weight, and coating ratio, but also on the weight gain with water sealing, the depth of dyed color, and the apparent density of the anodic film.

Experimental Procedure

High purity aluminum sheet, 0.5 mm thick, having the following percentage composition, was employed:

Fe 0.09, Si 0.04, Cu < 0.01, Mn < 0.01, Al 99.87 (by diff.)

Sets of four panels, each 5 x 15 cm with a small hole drilled at one end, were bolted about 3.5 cm apart and parallel to each other on an aluminum anodizing rack. A glass battery jar (16 x 20 x 26 cm) contained the electrolyte. The cathode, a U-shaped lead sheet, hung from the two opposite sides of the jar. Air agitation and water cooling were provided by glass and lead coils immersed in the solution. The jar was set in a large water bath with air agitation and water cooling coils, and with a thermoregulator - controlled electric immersion heater. The electrolyte temperature was maintained to within ±0.1°C of the set value.

Series of experiments were carried out anodizing in sulfuric acid solutions of 5, 15, 30, and 50% by weight at 10.1, 21.1, 30.4, and 50.2°C[2] for periods of 2, 5, 10, 30, and 60 min at 1.7 amp/dm² with a moderate degree of air agitation. A duplicate 30 min set was prepared for determination of the dissolution rate of the oxide coating. Another series measured the effect of air agitation under one set of conditions.

Panels were cleaned and oxide stripped (ASTM B-137-45) prior to weighing (W_1). Electroplating

[1] Manuscript received October 16, 1953. This paper was prepared for delivery before the Boston Meeting, October 2 to 7, 1954.

[2] For convenience designated as 10°, 21°, 30°, and 50° in further references.

stopoff tape was applied before and removed after anodizing to expose 1 dm² of surface. Current connection was made to the rack prior to immersion and disconnected after removal from the electrolyte. Panels were weighed after anodizing (W_2). One panel from each set was immersed in a dye solution (National Alizarine Sapphire SE, 4 g/l, 65°C, *p*H 6.5) for 5, 5, 10, 10, and 20 min for the 2, 5, 10, 30, and 60 min anodized panels, respectively. These periods were long enough to produce relatively complete dye takeup. The colored panels were sealed in boiling de-ionized water (*p*H 6.0 ± 0.2) for a period equal to the anodizing time and then weighed (W_4). Dyed panels were mutually compared and assigned a color rating ranging from 0, no color to 8, heavy color. Panels were oxide stripped, with customary confirmation of complete oxide removal and weighed (W_3).

The oxide film thickness was determined by standard metallographic technique on a thin strip cut from across the middle of one of the dyed 30 min anodized panels. The coating weights per square centimeter in the upper and lower sections were noted by weighing (W_4), oxide stripping, and reweighing (W_3). Apparent film density for the sealed coating was calculated.

The dissolution rate of the oxide coating in the electrolyte was determined by weighing (W_2) the panels from the duplicate 30 min sets and re-immersion in the electrolyte in which they had been anodized under the conditions that had prevailed during anodizing. Individual panels were removed after different immersion periods and weighed (W_5), stripped, and reweighed (W_3). The coating weight and metal loss with this set confirmed the values of the other set but were not included in the results recorded below.

The time of the shortest period of immersion decreased with rise in electrolyte temperature and, to a lesser extent, concentration. The first panels were removed after 5, 2, and 1 min from the electrolytes at 10° and 21°, 30° and 50°C, respectively. The time was reduced to 10 sec with the 30 and 50% acid at 50°C.

The effect of current density was examined in a second series of experiments, employing the procedure listed above, and anodizing in 15% by weight sulfuric acid solution at 21°, 30°, and 50°C at current densities of 0.5, 1.7, 3.6, and 6.2 amp/dm² for periods of 2, 5, 10, and 30 min. At the two higher current densities the panel size was proportionately reduced to permit anodizing with the current employed at 1.7 amp/dm² and so avoid an increased heating effect. Attempts to use 12 amp/dm² produced nonuniform growth of the anodic film with "burning" at points and edges, and results obtained are not recorded. A brief series was done with 5, 30, and 50% acid at 21°C and 3.6 amp/dm². Results obtained with the 5% solution are not listed because of the "burning" encountered.

The following values were determined as indicated:

Metal loss	W_1-W_3
Coating weight	W_2-W_3
Coating ratio	Coating weight/metal loss
Sealing weight gain*	W_4-W_2
Unit sealing	1000 × Sealing weight gain/coating weight
Coating dissolved by electrolyte	W_2-W_5
Apparent density	$\frac{\text{Coating weight (mg/cm}^2) \times 10}{\text{Film thickness } (\mu)}$

* Includes the relatively small weight gain on dyeing.

Adequate cold water rinses were provided after all solution treatments. No allowance was made for water, sulfuric acid, metal constituents, or aluminum salts in the coating. Under all conditions the bath voltage remained approximately constant during the anodizing period. Values reported are the average for the four panels of each set, except with the 30 min anodized series where they are based on three panels only. Individual panel results generally showed good agreement; otherwise the work was repeated. Values for dyed color, sealing weight gain, and density are based on single panel results.

Experimental Results

Appearance of anodic coatings.—A wide variety of coatings was produced with broad differences in their thickness and other characteristics. The two extremes were (*a*) a patchy "burnt" coating produced at 10°C with 5% acid, and (*b*) heavy chalking found at 30° and 50°C. Anodizing under the former conditions quickly formed a thin film with, it is believed, relatively high resistance over the entire surface. This was accompanied by the growth of a thicker film of a different type at many scattered points which were usually close to the bottom and lower side edges of the panel. Current density at such points was higher than elsewhere, affecting the local electrolyte temperature, and resulting in uneven and irregular coating formation. With continued anodizing these points grew together and finally spread over much of the surface. Dyed panels from this series became colored only in the areas with heavier deposit. Microscopic examination showed two distinct layers in the coating. Numerous pit-like points were visible in many of these patches with a center depression surrounded by concentric circles due to crazing. The pit depths were estimated as high as 10 μ. Current densities over 6.2 amp/dm² tended to produce even more pronounced "burning" at particular points or areas.

Air agitation.—Increased air agitation produced a slight rise in the coating weight and coating ratio due to its effect in lowering the electrolyte temperature at the coating-solution interface, and thus decreasing the loss of oxide by chemical dissolution.

Metal loss.—Metal loss values were approximately constant for passage of constant electric charge, regardless of variations in electrolyte temperature, concentration, or current density, and agreed closely with the calculated values.

Tosterud and Mason (8) found that anodizing in a 15% sulfuric acid bath at 27°–32°C takes place with an anodic metal dissolution efficiency of close to 100%, but suggested that at higher bath temperatures the aluminum may react by chemical, in addition to electrochemical, action so increasing the apparent efficiency to over 100%. Results indicate that with the high purity aluminum employed there is no significant chemical solution of the metal or anodic liberation of oxygen during anodizing with 5 to 50% sulfuric acid over the 10°–50°C range with current densities up to 6.2 amp/dm².

Coating weight.—Coating weight increases with anodizing time to a maximum value, which then remains approximately constant. The time required

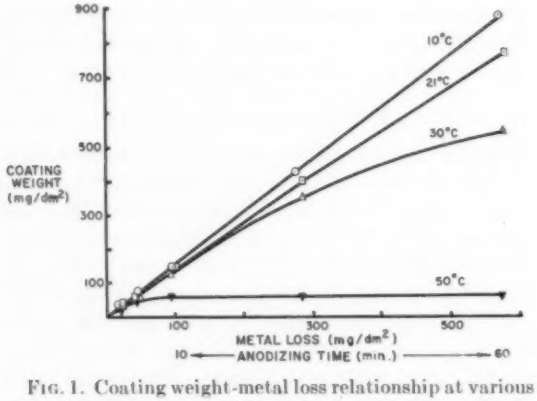

FIG. 1. Coating weight-metal loss relationship at various electrolyte temperatures (15% sulfuric acid, 1.7 amp/dm²).

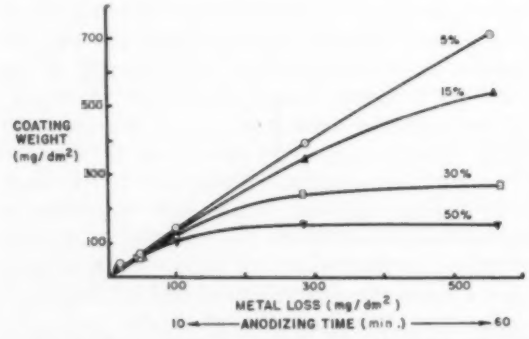

FIG. 2. Coating weight-metal loss relationship at various sulfuric acid concentrations (30°C, 1.7 amp/dm²).

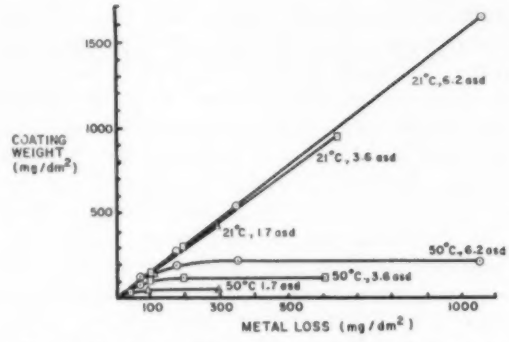

FIG. 3. Coating weight-metal loss relationship at various current densities and temperatures (15% sulfuric acid).

to attain this maximum is lowered by higher electrolyte concentration, increased electrolyte temperature, and lowered current density, as illustrated in Fig. 1, 2, and 3. Choice of suitably low temperature and concentration provides linear growth of coating weight for anodizing periods of 60 min or longer.

Increased current density (Fig. 3) raises the coating weight, but the effect is less striking than that of lowered electrolyte temperature or decreased electrolyte concentration, particularly the former between 21° and 30°C.

The great influence of anodizing conditions is illustrated by the broad range of coating weights and thicknesses obtained. For instance, the 30 min coatings vary from 10 mg/dm² or 0.6 μ thickness (50% acid, 50°C, and 1.7 amp/dm²) to 1622 mg/dm² or 66 μ thickness (15% acid, 21°C, and 6.2 amp/dm²).

Coating ratio.—Under the conditions employed the coating ratio decreases with increased anodizing time, greater electrolyte concentration, higher electrolyte temperature, and lowered anodizing current density. This is illustrated by Fig. 4 and 5, showing the fall in coating ratio with increased metal loss (i.e., prolonged anodizing) under various conditions at 21° and 50°C. These effects are due, as has been pointed out (3), to changes in the dissolution rates of the oxide film, produced by an increase in the surface area exposed to attack, a rise in the dissolving power of the electrolyte at higher concentrations and temperatures, or a slower formation rate, and thus a relatively greater degree of attack. The influence of these factors on coating ratio is much larger at higher electrolyte concentrations and temperatures.

Under some conditions of higher current density and lower temperature (Fig. 5) the coating ratio, after an initial fall, remains almost constant during further anodizing. In no case was there a rise in coating ratio as reported (7) for more extreme conditions.

The coating ratios varied from 0.01 (60 min, 50%

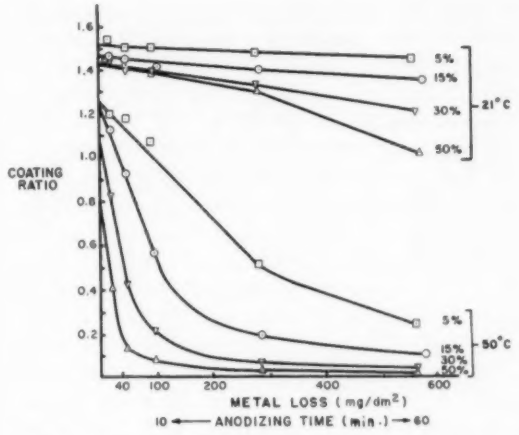

FIG. 4. Coating ratio vs. metal loss at various electrolyte concentrations and temperatures (1.7 amp/dm²).

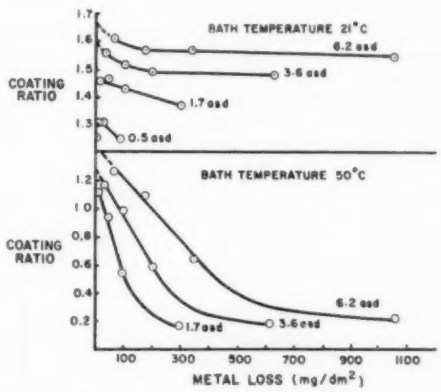

FIG. 5. Coating ratio vs. metal loss at various current densities and electrolyte temperatures (15% sulfuric acid).

acid, 50°C, and 1.7 amp/dm²) to 1.61[3] (2 min, 15% acid, 21°C, at 6.2 amp/dm²). The highest value reported by Mason and Slunder was approximately 1.51. Values as high as 1.90 have been secured by Mason and Fowle (7) by anodizing in 15% sulfuric acid at low temperature and high current density (1.1°C, 7.8 amp/dm²). The coating ratio increased with prolonged anodizing under these extreme conditions.

Chemical dissolution of the anodic coating.—Under all conditions the weight loss increased with longer immersion times but at a decreasing rate due to the reduction in the area of coating exposed to electrolyte attack. Dissolution of the thin coatings formed at 50°C, particularly in the more concentrated acid, was very rapid. For instance, the 50% acid coating was removed completely in 30 sec.

The initial dissolution rates (Fig. 6), determined under conditions prevailing during anodizing except for the absence of current, may be taken as an approximation to the coating dissolution rate during anodizing. Values rise with higher bath temperature and acid concentration and range from 0.6 to 30 mg/dm²/min, an increase of fiftyfold in the dissolution rate. This difference explains the wide variations in coating weights and other film properties with anodizing conditions. Calculation of the specific dissolution rates (rates per gram of coating weight) gave a 3000-fold range of values, indicating the wide choice in electrolyte conditions possible.

Sealing weight gain.—The sealing weight gain rose with increased anodizing time at electrolyte temperatures of 10°, 21°, and 30°C. At 50°C gains were more constant in value due to the smaller and less regular effect of continued anodizing on the coating weight. The sealing weight gain would be expected to increase with heavier coatings and/or with an increase in their porosity.

Unit sealing values are dependent in large degree only on porosity. Values increased with greater coating weights. The effect was more pronounced at higher electrolyte temperatures (9) (Fig. 7) and lower current densities (Fig. 8).

Color rating of dyed panels.—The color of the dyed panels covered a wide range extending from ab-

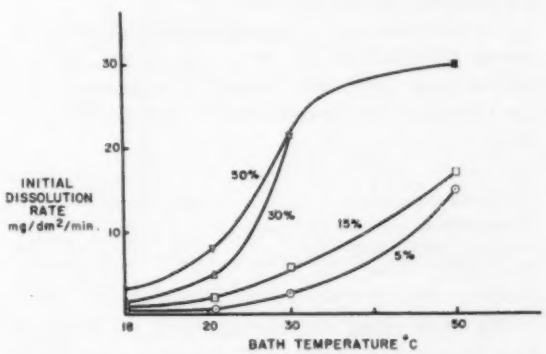

FIG. 6. Dissolution rates of anodic coatings in sulfuric acid electrolyte (panels anodized for 30 min).

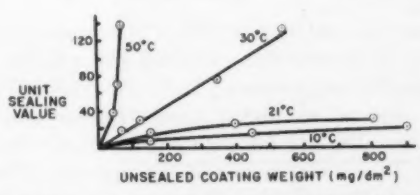

FIG. 7. Unit sealing values vs. unsealed coating weights at various electrolyte temperatures (15% sulfuric acid, 1.7 amp/dm²).

[3] A special attempt was made to obtain a high coating ratio. A 5% acid solution chilled to 6°C was employed with a current density of 5.4 amp/dm². The current flow concentrated on the two lower edges, and thus produced a nonuniform coating. The coating ratio, in spite of high current density and decreased dissolution rate, was only 1.68.

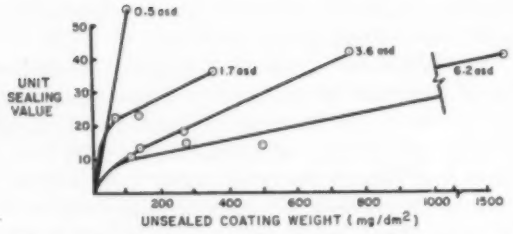

FIG. 8. Unit sealing values vs. unsealed coating weights at various current densities (15% sulfuric acid, 21°C).

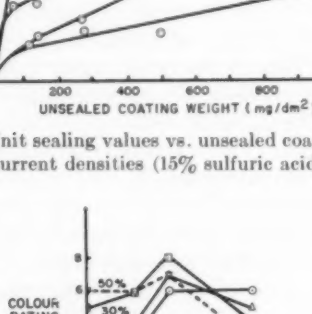

FIG. 9. Effect of electrolyte temperature on the color of dyed anodic coatings (panels anodized for 30 min at 1.7 amp/dm²).

sence of color to a very heavy blue black. The color rating (like the unit sealing values) in general rose with prolonged anodizing, higher acid temperatures, and concentrations. An increase in the temperature (Fig. 9) from 21° to 30°C produced a much darker color. At higher temperatures, the color became lighter. The color rating increased, but only slightly with higher current density.

The following typical example illustrates the qualitative relationships between coating weight, unit sealing value, and color ratings for panels anodized for 10 min in the four electrolyte concentrations at 30°C.

Acid concentration	5%	15%	30%	50%
Color rating	3	4	5	6
Coating weight (mg/dm²)	137	127	117	109
Unit sealing value	13	31	45	144

The color rating steadily increased, accompanied by a large gain in unit sealing due to increased coating porosity. This was in spite of the lowering in coating weight which would tend to lower the color rating.

Apparent coating density.—The apparent coating density decreased with increased acid concentration and higher temperature (Table I). The effect was more marked at higher concentrations and temperatures. Density fell with higher current densities rather than rising as would be expected. This was due probably to the much greater coating thickness produced as the current density increased. The influence of this variable was not determined. The density of the sealed films varied from 2.68 to 1.5 due to differences in the characteristics, particularly the porosity of the anodic coatings.

TABLE I. *Apparent density of sealed anodic coatings* (30 min anodized panels)

Sulfuric acid electrolyte		Current density, amp/dm²	Film thickness, μ	Apparent density
Temp, °C	Conc, % by wt			
10	15	1.7	18.1	2.54
	30		16.8	2.53
	50		19.0	2.39
21	5	1.7	16.3	2.66
	15		16.5	2.64
	30		17.1	2.36
	50		18.7	2.08
30	5	1.7	15.6	2.68
	15		15.0	2.53
	30		15.6	2.04
	50		10.0	1.93
50	5	1.7	9.7	1.9
	15		3.4	1.8
			1.5	1.5
21	15	0.5	4.1	2.8
		1.7	14.0	2.68
		3.6	29.7	2.66
		6.2	66.0	2.46
30	15	1.7	14.9	2.50
		3.6	30.5	2.41
		6.2	58.5	2.18
50	15	1.7	2.5	2.1
		3.6	6.5	2.1
		6.2	12.3	2.1

DISCUSSION

Anodic Film Growth

The growth rate of the anodic film on high purity aluminum in sulfuric acid solutions is the resultant of two opposing factors: the electrochemical growth of aluminum oxide and the chemical dissolution of the film. The former depends upon current density and anodizing time, but is influenced by changes in anodizing conditions. The dissolution of the coating is affected by the electrolyte composition and concentration, bath temperature, degree of air agitation, and the extent of oxide surface present. With continued anodizing, the dissolution rate rises finally to equal the growth rate. From this point the coating weight remains constant (Fig. 2; 30 and 50% acid curves).

However, this picture is oversimplified and does not include the effect of possible variations in film structure, film composition, and anodic reactions

with changes in anodizing conditions. It also neglects the mutual dependence of some of the anodizing variables. For instance, current density affects not only the rate of film formation, but also the temperature of the liquid film in the pores and on the external surface of the anodic coating (10). A great part of the anode-to-cathode electrical resistance is in the pores, particularly at their base where the so-called "barrier layer" is formed. This layer is believed to be nonporous and thus possesses high resistance. The heating effect at this point should be considerable and will increase with the square of the current. This heat can be dissipated only slowly and, thus, the local temperature will be expected to be considerably higher than the bath temperature. Any increase in current density will consequently increase the local temperature and raise the rate of chemical dissolution in addition to its other effects. Under certain extreme anodizing conditions increased current density may reduce the rate of chemical dissolution of the oxide at the base of the pores due, it is claimed (7), to the build-up of solution products. This has been suggested to explain the rise in coating ratio with prolonged anodizing at low temperatures (1°–10°C) and high current densities (3.9–7.8 amp/dm²).

Coatings can be obtained with a wide range of film properties by a choice of anodizing variables. Many anodic films of given thickness and porosity can be produced by several different combinations of anodizing conditions. Changes in electrolyte temperature have a relatively greater effect on film properties than variations in other conditions, particularly as the temperature rises above 25°C.

Anodic Reactions

The reactions that may take place during anodic treatment of high purity aluminum in sulfuric acid are as follows: (*a*) electrochemical dissolution of aluminum and formation of oxide; (*b*) electrochemical dissolution of aluminum and formation of soluble aluminum salts; (*c*) electrochemical formation and evolution of oxygen; (*d*) chemical dissolution of oxide by the electrolyte; (*e*) chemical dissolution of aluminum and liberation of hydrogen.

It has been shown that under the wide range of anodizing conditions studied the metal loss is constant and approximates the theoretical value. This proves that reactions (*c*) and (*e*) do not occur to any significant extent under these conditions. Thus, the anodic formation of the oxide coating includes reaction (*a*) to form the oxide, (*d*) to form the pores which permit continued anodizing, and (*b*) which, if present, reduces the coating formation efficiency and the coating ratio. The possibility of (*b*) has been mentioned by others (2, 3, 5) but not verified experimentally.

The coating ratio may be represented as follows:

$$\text{Coating ratio} = \frac{\text{Weight of coating formed} - \text{Weight of coating dissolved}}{\text{Metal loss}}$$

The ratio at the moment of initiating anodizing is of special interest. At this point chemical dissolution of the film is just beginning and has its minimum effect on the coating weight. If the dissolution were negligible, the coating ratio would approach the following value.

$$\text{Coating ratio} = \frac{\text{Weight of coating formed}}{\text{Metal loss}}$$

that is, the actual ratio of two processes, the formation of oxide and the accompanying dissolution of aluminum.

Mason and Slunder (3) employed simple extrapolation of the coating ratio-metal loss curves to zero metal loss to yield a value which they employed to calculate the weight of the coating dissolved in the electrolyte during anodizing. This value has been determined for the various anodizing conditions reported above and designated the "CR_0" value, the "coating ratio at zero metal loss."

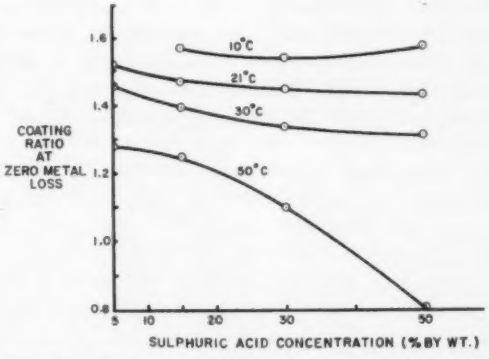

FIG. 10. Effect of electrolyte concentration on coating ratios at zero metal loss at various temperatures (1.7 amp/dm²).

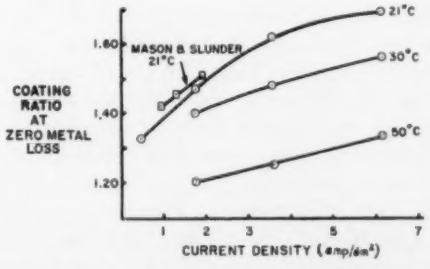

FIG. 11. Effect of current density on coating ratios at zero metal loss at various temperatures (15% sulfuric acid).

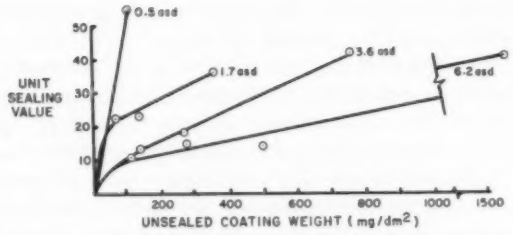

FIG. 8. Unit sealing values vs. unsealed coating weights at various current densities (15% sulfuric acid, 21°C).

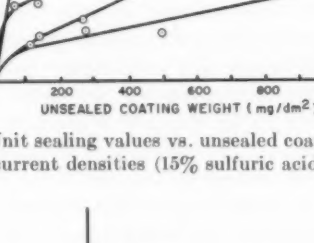

FIG. 9. Effect of electrolyte temperature on the color of dyed anodic coatings (panels anodized for 30 min at 1.7 amp/dm²).

sence of color to a very heavy blue black. The color rating (like the unit sealing values) in general rose with prolonged anodizing, higher acid temperatures, and concentrations. An increase in the temperature (Fig. 9) from 21° to 30°C produced a much darker color. At higher temperatures, the color became lighter. The color rating increased, but only slightly with higher current density.

The following typical example illustrates the qualitative relationships between coating weight, unit sealing value, and color ratings for panels anodized for 10 min in the four electrolyte concentrations at 30°C.

Acid concentration	5%	15%	30%	50%
Color rating	3	4	5	6
Coating weight (mg/dm²)	137	127	117	109
Unit sealing value	13	31	45	144

The color rating steadily increased, accompanied by a large gain in unit sealing due to increased coating porosity. This was in spite of the lowering in coating weight which would tend to lower the color rating.

Apparent coating density.—The apparent coating density decreased with increased acid concentration and higher temperature (Table I). The effect was more marked at higher concentrations and temperatures. Density fell with higher current densities rather than rising as would be expected. This was due probably to the much greater coating thickness produced as the current density increased. The influence of this variable was not determined. The

TABLE I. *Apparent density of sealed anodic coatings* (30 min anodized panels)

Sulfuric acid electrolyte		Current density, amp/dm²	Film thickness, μ	Apparent density
Temp, °C	Conc, % by wt			
10	15	1.7	18.1	2.54
	30		16.8	2.53
	50		19.0	2.39
21	5	1.7	16.3	2.66
	15		16.5	2.64
	30		17.1	2.36
	50		18.7	2.08
30	5	1.7	15.6	2.68
	15		15.0	2.53
	30		15.6	2.04
	50		10.0	1.93
50	5	1.7	9.7	1.9
	15		3.4	1.8
			1.5	1.5
21	15	0.5	4.1	2.8
		1.7	14.0	2.68
		3.6	29.7	2.66
		6.2	66.0	2.46
30	15	1.7	14.9	2.50
		3.6	30.5	2.41
		6.2	58.5	2.18
50	15	1.7	2.5	2.1
		3.6	6.5	2.1
		6.2	12.3	2.1

density of the sealed films varied from 2.68 to 1.5 due to differences in the characteristics, particularly the porosity of the anodic coatings.

DISCUSSION

Anodic Film Growth

The growth rate of the anodic film on high purity aluminum in sulfuric acid solutions is the resultant of two opposing factors: the electrochemical growth of aluminum oxide and the chemical dissolution of the film. The former depends upon current density and anodizing time, but is influenced by changes in anodizing conditions. The dissolution of the coating is affected by the electrolyte composition and concentration, bath temperature, degree of air agitation, and the extent of oxide surface present. With continued anodizing, the dissolution rate rises finally to equal the growth rate. From this point the coating weight remains constant (Fig. 2; 30 and 50% acid curves).

However, this picture is oversimplified and does not include the effect of possible variations in film structure, film composition, and anodic reactions

with changes in anodizing conditions. It also neglects the mutual dependence of some of the anodizing variables. For instance, current density affects not only the rate of film formation, but also the temperature of the liquid film in the pores and on the external surface of the anodic coating (10). A great part of the anode-to-cathode electrical resistance is in the pores, particularly at their base where the so-called "barrier layer" is formed. This layer is believed to be nonporous and thus possesses high resistance. The heating effect at this point should be considerable and will increase with the square of the current. This heat can be dissipated only slowly and, thus, the local temperature will be expected to be considerably higher than the bath temperature. Any increase in current density will consequently increase the local temperature and raise the rate of chemical dissolution in addition to its other effects. Under certain extreme anodizing conditions increased current density may reduce the rate of chemical dissolution of the oxide at the base of the pores due, it is claimed (7), to the build-up of solution products. This has been suggested to explain the rise in coating ratio with prolonged anodizing at low temperatures (1°–10°C) and high current densities (3.9–7.8 amp/dm²).

Coatings can be obtained with a wide range of film properties by a choice of anodizing variables. Many anodic films of given thickness and porosity can be produced by several different combinations of anodizing conditions. Changes in electrolyte temperature have a relatively greater effect on film properties than variations in other conditions, particularly as the temperature rises above 25°C.

Anodic Reactions

The reactions that may take place during anodic treatment of high purity aluminum in sulfuric acid are as follows: (*a*) electrochemical dissolution of aluminum and formation of oxide; (*b*) electrochemical dissolution of aluminum and formation of soluble aluminum salts; (*c*) electrochemical formation and evolution of oxygen; (*d*) chemical dissolution of oxide by the electrolyte; (*e*) chemical dissolution of aluminum and liberation of hydrogen.

It has been shown that under the wide range of anodizing conditions studied the metal loss is constant and approximates the theoretical value. This proves that reactions (*c*) and (*e*) do not occur to any significant extent under these conditions. Thus, the anodic formation of the oxide coating includes reaction (*a*) to form the oxide, (*d*) to form the pores which permit continued anodizing, and (*b*) which, if present, reduces the coating formation efficiency and the coating ratio. The possibility of (*b*) has been mentioned by others (2, 3, 5) but not verified experimentally.

The coating ratio may be represented as follows:

$$\text{Coating ratio} = \frac{\text{Weight of coating formed} - \text{Weight of coating dissolved}}{\text{Metal loss}}$$

The ratio at the moment of initiating anodizing is of special interest. At this point chemical dissolution of the film is just beginning and has its minimum effect on the coating weight. If the dissolution were negligible, the coating ratio would approach the following value.

$$\text{Coating ratio} = \frac{\text{Weight of coating formed}}{\text{Metal loss}}$$

that is, the actual ratio of two processes, the formation of oxide and the accompanying dissolution of aluminum.

Mason and Slunder (3) employed simple extrapolation of the coating ratio-metal loss curves to zero metal loss to yield a value which they employed to calculate the weight of the coating dissolved in the electrolyte during anodizing. This value has been determined for the various anodizing conditions reported above and designated the "CR_0" value, the "coating ratio at zero metal loss."

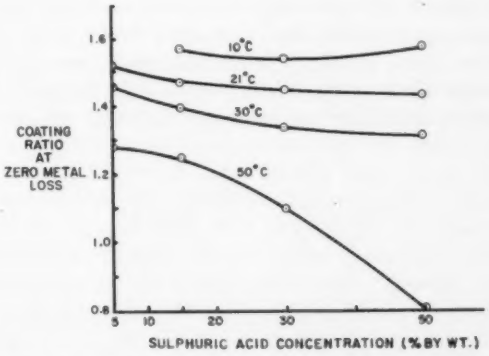

FIG. 10. Effect of electrolyte concentration on coating ratios at zero metal loss at various temperatures (1.7 amp/dm²).

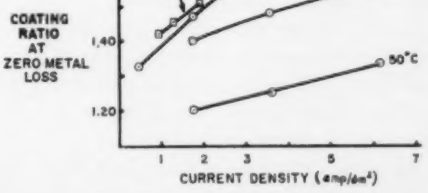

FIG. 11. Effect of current density on coating ratios at zero metal loss at various temperatures (15% sulfuric acid).

The CR_0 values obtained are plotted in Fig. 10 and 11 as functions of electrolyte concentration and current density, respectively. The former has a relatively small effect on the CR_0 at the three lower temperatures, but at 50°C the value drops severely with higher concentration.

As expected, the CR_0 value rises with increased current density (Fig. 11). At 21°C the rate of increase lessens as a current density of 6.2 amp/dm^2 is approached, and suggests that still higher current densities probably would cause only a slight further increase. Three CR_0 values taken from Mason and Slunder (3) are plotted in Fig. 11, and show good agreement with the other results particularly in view of the slightly different anodizing conditions employed.

The CR_0 values range from 0.80 to 1.67. Even the highest figure is considerably below the maximum theoretical value of 1.89 which is based on the premise that the sole anodic reaction is the electrochemical conversion of aluminum into aluminum oxide. This figure should be increased if allowance is made for the sulfate or water contained therein. Mason and Fowle (7) have mentioned a value of 2.2, but the figure will vary with anodizing conditions due to variations in the sulfate and/or water content.

The effect of chemical dissolution of the oxide film on the CR_0 values will vary with the anodizing conditions, but probably is far from negligible and, under some conditions, quite appreciable. This will lower these values and affect the accuracy of calculated weights of the coating chemically dissolved at various anodizing periods based on such values.

Dissolution rates derived from such calculations should be comparable with initial dissolution rates measured as described above at several anodizing periods. If agreement is lacking the CR_0 value may be varied until such is secured. The modified CR_0 value may be a more accurate measure of the coating ratio at zero metal loss than the extrapolated figure. The initial dissolution rates listed above were obtained only on the 30 min coatings and so permitted checking at this one point only. This technique was applied to one set of conditions and gave fair agreement at 21° and 30°C and poor agreement at 50°C.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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An Interpretation of the Significance of the Potentials of Passive Iron[1]

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ABSTRACT

The steady-state value of the passive potential of iron in anodic inhibitors forming hydrated oxide corrosion products with ferrous ions becomes less noble with increasing *p*H and with increasing inhibitor concentration. Values of passive potentials in phosphate solutions become more noble with increasing *p*H. The effect of surface pretreatment and of the addition of small amounts of chloride on the passive potentials is more pronounced at high *p*H values. Increasing the oxygen concentration of the solutions results in a shift in the steady-state values of the passive potentials in the more noble direction. An explanation of these effects, based on the oxide film theory of anodic inhibition, is advanced.

Introduction

The electrode potential of iron has long been considered to give some approximate indication of its behavior toward aqueous solutions. For instance, when iron is corroding freely in an aqueous solution, its potential is often of the order of -0.4 to -0.5 v;[2] when corrosion is inhibited by an efficient anodic inhibitor the potential of iron usually will be of the order of zero volts or more noble. In this connection the ennobled potentials of passive iron are frequently referred to as "passive potentials."

Passive potentials are encountered on iron exposed to solutions of efficient anodic inhibitors. Any interpretation of these potentials depends to a considerable extent on which of the several theories of anodic inhibitors is adopted. Supporters of the precipitation theory (1) have attributed the noble values of the passive potentials to the high degree of anodic polarization resulting from the precipitation of insoluble iron corrosion products at anodic areas or to an increase in the internal resistance of the local corrosion cells for the same reason (2). Until recently, supporters of other theories of anodic inhibition have made no comparable attempt to interpret passive potentials. Recently, however, Uhlig and Geary (3) measured the potentials of electrolytic iron in distilled water containing between 0 and 2.5×10^{-3} moles/liter of chromate. On plotting change in potential against chromate concentration, a curve, similar in form to a Langmuir isotherm, was obtained. The authors, using the electrostatic theory of potential, suggested that the change in potential was directly proportional to the amount of chromate adsorbed and that the maximum or most noble value of potential measured was proportional to the maximum amount of chromate adsorbed.

However, the main purpose of this article is not to argue the relative merits of different theories of anodic inhibition but to determine how an extension of the oxide-film theory of anodic inhibition (4–11) can account, at least in a semiquantitative manner, for passive potentials and their variation with different conditions in solution.

Values of the passive potentials would appear from the literature to be rather irreproducible and few definite trends have been reported previously for iron. Corrosion investigators have long been interested in the theoretical aspects of corrosion potentials, and Müller and others (12–14) derived equations relating the corrosion potential to the potentials of the local anodes and cathodes, the resistance of the surface oxide film, and that of the pores in its film. It was shown that increasing the resistance of the pores in the oxide film by some type of film repair process (either precipitation of corrosion product or formation of oxide) resulted in a shift in potential in the positive (more noble) direction. At the time these equations were derived, however, the chemistry of the reactions taking place between iron and anodic inhibitors was not well understood and this prevented the investigators from carrying their calculations further.

Recently it has been found possible to determine passive potentials of iron in solutions of anodic inhibitors in a reasonably reproducible manner (8). It was found that, with a very few exceptions, the steady values of the passive potentials became more negative (active) with increasing *p*H in anodic in-

[1] Manuscript received August 23, 1954. This paper was prepared for delivery before the Boston Meeting, October 2 to 7, 1954.

[2] All potentials in this paper are expressed on the standard hydrogen scale.

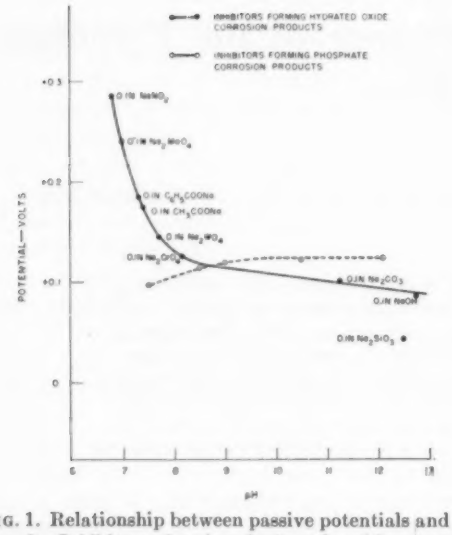

FIG. 1. Relationship between passive potentials and *p*H. ●——●, Inhibitors forming hydrated oxide corrosion products; ○- - -○, inhibitors forming phosphate corrosion products.

hibitors which can form hydrated iron oxide corrosion products, but that they became more positive with increasing dilution of the same inhibitor solution (8). This paper describes an extension of these studies to include such variables as the surface condition of the iron, the oxygen content of the solution, and the addition of chloride ions. An attempt is also made to explain these well-defined trends in the passive potential and also to account for the exceptions to these trends.

EXPERIMENTAL

Materials and methods.—The iron used was in the form of annealed sheet 0.02 cm thick; its analysis was described previously (6). Specimens cut from this sheet were degreased with benzene and cut to size so that an area 2.5 cm x 0.5 cm was exposed to the solution under examination. All solutions were made up with C.P. chemicals and distilled water. The apparatus used for the potential determinations and the experimental method were described in a previous paper (8).

Results

Potential-time curves[3] were determined previously (8) on iron specimens freshly abraded with 3/0 emery paper in 0.1*N* solutions of sodium nitrite, molybdate, tungstate, benzoate, acetate, chromate, carbonate, hydroxide, and silicate. These inhibitors are of the type that, at a concentration of 0.1*N*, form hydrated oxide corrosion products on reaction with ferrous ions.

[3] All potential-time curves were determined in triplicate.

In this investigation, potential-time curves were determined on iron immersed in five 0.1M phosphate solutions having *p*H values within the range 7.5–12.1. These solutions at a concentration of 0.1M form corrosion products of ferrous or ferric phosphate.

Fig. 1 summarizes the relation between the steady-state values of the passive potentials and the *p*H values of the nine 0.1*N* inhibitor solutions and those of the five 0.1M phosphate solutions. The steady value is the value of the potential after five days and changes little with increasing time.

Fig. 2 shows the relation between passive potential and concentration of sodium nitrite, acetate, and chromate. In all cases the potential becomes more noble with increasing dilution, provided passivity is maintained.

Experiments were next carried out to determine the effect of surface treatment on the passive potential. The surface treatments investigated were as follows.

(*A*) The air-formed oxide films were destroyed by immersing degreased specimens in 0.1*N* hydrochloric acid for 1 min (15); specimens were then washed rapidly in distilled water and immediately exposed to the passivating solution.

(*B*) Specimens were abraded with 3/0 emery paper and then swabbed with benzene, dried in acetone, and exposed to the passivating solution.

These two surface treatments were selected because they gave consistently the most reproducible results. The effect of these surface treatments was investigated in decinormal solutions of sodium hydroxide, benzoate, and disodium phosphate. The results (Fig. 3) show that iron in the comparatively

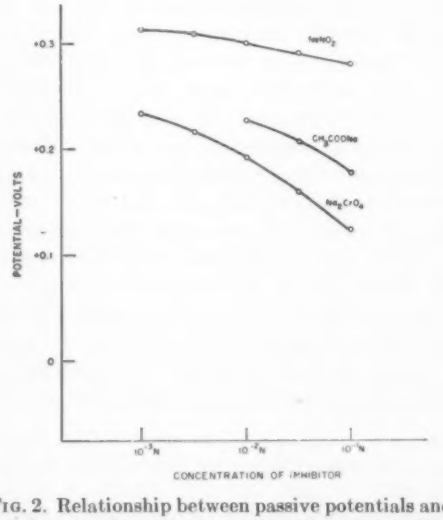

FIG. 2. Relationship between passive potentials and concentration of sodium nitrate, sodium chromate, and sodium acetate.

"film-free" condition, i.e., after treatment with hydrochloric acid, consistently gives lower values of potential than when it carries an imperfect oxide film as after abrasion and that the difference in potential increases with increasing *p*H.

Experiments were also carried out to determine the effect of adding 10 ppm of chloride ion in the form of potassium chloride to decinormal sodium hydroxide, sodium benzoate, and disodium phosphate. The results (Fig. 4) show that the addition of chloride to disodium phosphate and sodium hydroxide causes a shift in potential in the negative direction and that the effect increases with a rise in *p*H.

Since the access of air to the solution is influenced by the ratio of surface area of the solution to its volume, experiments were carried out to determine the effect of the area of surface at constant volume of solution on the passive potential in 0.1*N* sodium hydroxide using specimens having a surface area of 2.5 cm². In the normal method of carrying out these experiments, the ratio of surface area of the solution to its volume is 33:300. Two additional tests were carried out under conditions of free access of the atmosphere to the solution. Ratios of surface area of the solution to volume were 44:300 and 229:300. The area of specimens exposed to the solution was the same (2.5 cm²) in each experiment. However, in experiments with a surface area of 229 cm², specimens were exposed with their short axes vertical rather than their long axes as in all previous experiments. Results are shown in Fig. 5 from which it may be seen that increasing the ratio of surface area of the solution to the volume results in a shift in potential in the positive, more noble, direction.

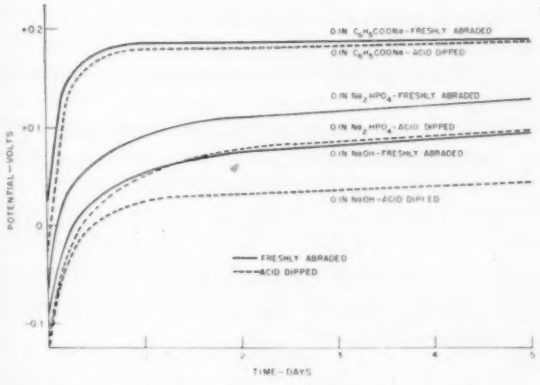

FIG. 3. Effect of surface pretreatment on passive potentials.

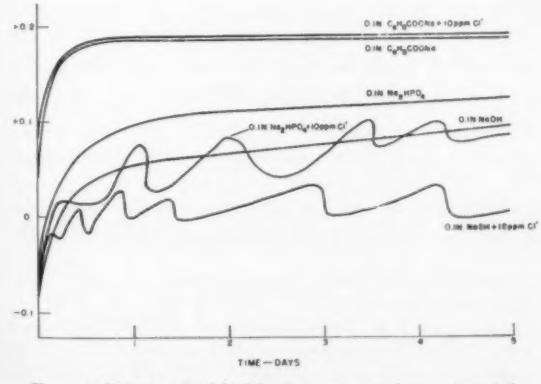

FIG. 4. Effect of chloride ion on passive potentials

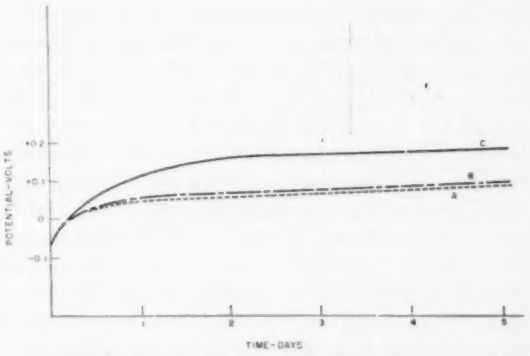

FIG. 5. Effect of surface area of the solution on passive potentials. Curve A, surface area of solution: volume = 33:300; curve B, surface area of solution: volume = 44:300; curve C, surface area of solution: volume = 229:300.

DISCUSSION

The anodic inhibitors investigated above may be divided into two classes, viz.: (*a*) those inhibitors which at a concentration of 0.1*N* form hydrated iron oxides when reacted with ferrous ions and oxygen; and (*b*) those inhibitors which at a concentration of 0.1M form ferrous or ferric phosphate when reacted with ferrous ions and oxygen.

With inhibitors of the first class, values of the passive potentials of iron become progressively less noble with increasing *p*H of the inhibitor (Fig. 1) with the exception of sodium silicate.

With inhibitors of the second class the steady-state value of the passive potentials became progressively more noble with increasing *p*H (Fig. 1), exactly the opposite trend observed in inhibitors forming hydrated oxide corrosion products with ferrous ions. However, over the same *p*H range, change in potential was less than with inhibitors of the first class.

It is believed that the mechanism of inhibition for the inhibitors studied in this investigation is essentially similar (8). Inhibition is believed to be associated with oxygen dissolved in solution. The oxygen is believed first to adsorb on the iron surface and then to take part in a direct reaction with sur-

face iron ions to form a thin film of γ-Fe_2O_3 which is considered to grow to an equilibrium thickness in a manner similar to that by which oxide films grow on iron in dry air. Rate of growth is probably controlled by the rate of diffusion of iron ions and electrons through the film to the film/solution interface. The film is considered to prevent corrosion by stopping iron ions leaving the metal lattice and passing into solution. However, the formation of a protective film of γ-Fe_2O_3 is not instantaneous and, at discontinuities initially present in the film, very slow corrosion occurs. This corrosion is believed to be subject to a high degree of anodic polarization due to the small size of the discontinuities (anodic areas) in the oxide film.

In inhibitor solutions originally free from iron ions, iron can pass into solution as soluble ions. During this period, the oxide film is considered to be not only thickening, but also to be extending laterally and thus further reducing the size of the anodic areas. However, all inhibitor solutions considered here eventually react with a sufficiently high concentration of ferrous or ferric ion to form insoluble corrosion products, either of hydrated iron oxide or of hydrated iron phosphate. Thus, insoluble corrosion products will ultimately be formed at the discontinuities in the oxide film. The corrosion product is believed to greatly assist the achievement of a passive state by further reducing the rate at which iron ions pass into solution. However, these inclusions of corrosion product are not absolutely necessary for passivity since inhibition can be obtained in sodium cyanide and tartrate which prevent precipitation of corrosion product. The time taken for precipitation depends on the solubility product of the corrosion product, the rate of corrosion of the iron at discontinuities in the film, the *p*H of the solution and, in phosphates, the phosphate content of the solution. It has been suggested that the precipitation of corrosion products at discontinuities in the passivity film not only increases the anodic polarization, but also interferes with the lateral film growth of the oxide film (8). Thus, the time at which precipitation of corrosion product occurs should determine the size of the inclusions of corrosion product in the oxide film. Their permeability to the outward diffusion of hydrated ferrous ions will determine their final thickness, which appears to be greater than that of the oxide film (5).

For purposes of interpreting passive potentials, it is assumed that formation of oxide by direct interaction of dissolved oxygen with surface iron atoms makes no direct contribution to the potential of the specimen as normally measured. Thus, the passive potential is believed to be the potential of the very slow corrosion reaction leading to the formation of small inclusions of corrosion product in the passivity film. Therefore, the contribution of the oxide film on the passive potential is indirect in that it influences the size of the anodic areas and the size of the inclusions of corrosion product. The anodic reaction of this corrosion process is believed to be the passage of ferrous ions into solution at discontinuities in the oxide film and the cathodic reaction is primarily the reduction of dissolved oxygen at the surface of the oxide film. Since the anodic areas, even initially, are small, the cathodic area should be essentially constant. The passive potential is a mixed potential since both the anodic and cathodic polarization are appreciable.

The two main reactions taking place during the passivation of iron in anodic inhibitors are thus: (*a*) formation of a thin film of γ-Fe_2O_3 by direct interaction of the iron surface with dissolved oxygen; and (*b*) corrosion at initial discontinuities in the γ-Fe_2O_3 film leading eventually to the formation of small and relatively thick inclusions of corrosion-product (7).[4]

Reaction (*a*), the formation of the oxide film by dissolved oxygen, should be largely independent of *p*H and should depend only on the concentration of oxygen in solution and on the active mass of the iron. The rate of reaction (*b*), however, should be controlled largely by the environment surrounding the specimen.

Müller (14) has derived a general relationship for the potential of a metal partly covered with a protective oxide film. This relationship is

$$E = E_A(1 - K) + E_cK \qquad (I)$$

where E_A and E_c are the true potentials of the anode and cathode, respectively, E the measured compromise potential, and

$$K = \frac{R_p}{R_p + R_F} \qquad (II)$$

where R_F and R_p are the resistances of the film and of pores in the film, respectively. It can be seen that, as the resistance of the pores increases, the fraction K tends to unity and the potential moves in the cathodic direction. When R_p is infinitely large,

$$E = E_c \qquad (III)$$

Since the size of discontinuities in the oxide film is initially small, the film resistance and the cathodic

[4] Oxidizing inhibitors such as chromate, nitrate, tungstate, and molybdate are believed to have the ability to form some oxide at discontinuities in γ-Fe_2O_3 film (8) which accounts for their superior inhibitive powers. The great majority of oxide film is, however, believed to be formed by dissolved oxygen.

area can be considered to be constant. In the period before precipitation takes place in the pores

$$R_p = \frac{R_o L}{A} \qquad \text{(IV)}$$

where R_o is the specific resistance of the electrolyte, L equals the length of the pore in the film (approximately the thickness of the film), and A is the cross-sectional area. As film growth proceeds in the absence of precipitation, the lateral extension of the oxide film decreases the value of A and increases R_p. Thus, a relatively rapid initial increase in potential with time is observed for all anodic inhibitors (8). Later, corrosion products become precipitated in the pores, essentially fixing the size of the anodic areas, as suggested above. Equation (IV) shows that the smaller the size of the anodic areas the higher is the value of R_p and that of the potential. Of course, precipitation of corrosion product further increases the resistance of the pores and makes it more difficult for iron ions to pass into solution at these areas. The further gradual increase in the potential with time (6, 8) probably reflects the very slow thickening of the inclusions of corrosion product.

In the case of phosphate solutions, it has been shown that inclusions composed mainly of strengite ($FePO_4 \cdot 2H_2O$) are formed in the passivity films (10). The size of the inclusions (10) and the quantity of ferric phosphate (7) are less in trisodium phosphate (0.2×10^{-3} mg/cm^2 at pH = 12.1) than in disodium phosphate (0.6×10^{-3} mg/cm^2 at pH = 9.0). Evidently in these phosphate solutions ferric phosphate is more insoluble than lepidocrocite.

The formation of ferric phosphate can be expressed in equation form as follows

$$4Fe^{++} + 4H^+ + O_2 = 4Fe^{+++} + 2H_2O \qquad \text{(V)}$$

$$4Fe^{+++} + 4PO_4''' = 4FePO_4 \qquad \text{(VI)}$$

$$4Fe^{++} + 4PO_4''' + 4H^+ + O_2 = 4FePO_4 + 2H_2O \qquad \text{(VII)}$$

$$\text{or as } 4Fe^{++} + 4HPO_4'' + O_2 = 4FePO_4 + 2H_2O \qquad \text{(VIII)}$$

It is assumed in the following arguments that the ferrous ion concentration in solution determines the unpolarized potential of the anode (16, 17) and that the ferrous ion concentration is controlled by the precipitation of ferric phosphate. Accordingly, the basic anodic reaction is:

$$Fe \rightarrow Fe^{++} + 2\epsilon \qquad \text{(IX)}$$

The initial iron content of the solution is proportional to the rate at which the iron corrodes at discontinuities in the oxide film. According to Abbott and Bray (18) the $[PO_4''']$ concentration in aqueous solutions is given by the relationship

$$[PO_4'''] = \frac{K_1[HPO_4'']}{[H^+]} \qquad \text{(X)}$$

where $K_1 = 3.6 \times 10^{-13}$. Evidently $[PO_4]'''$ ions are present only in minor quantities in a 0.1M solution of so-called trisodium phosphate (pH = 12.1). This is supported by the absence of an inflection in the neutralization curve of phosphoric acid at a pH value of 12.1 (6). The solubility product of ferric phosphate is given by the product of the concentrations of $[Fe^{+++}]$ and $[PO_4''']$ ions in equilibrium with solid ferric phosphate. From equations (VII) and (X), the solubility product of ferric phosphate can be expressed in terms of concentrations of $[Fe^{++}]$, $[HPO_4'']$, and oxygen as follows

$$S_{FePO_4} = K_1K_2[Fe^{++}][HPO_4''][O_2]^{1/4} \qquad \text{(XI)}$$

where K_2 is the equilibrium constant of equation (V). Since, in the solutions under examination, $[HPO_4'']$ is approximately constant at 10^{-1}M, the time taken to reach the solubility product of ferric phosphate at constant oxygen concentration depends only on the rate of corrosion of the iron at discontinuities in the oxide film. The rate of corrosion should decrease with increasing pH of the bulk solution, and so the time elapsing before precipitation of ferric phosphate occurs should increase with increasing pH of the solution. Since it has been assumed that the formation of insoluble precipitates interferes with the lateral growth of the oxide film, this indicates that the size of the inclusion of corrosion product should decrease and that the anodic polarization and the value of the passive potential should increase with increasing pH in 0.1M phosphate solutions. This is demonstrated experimentally in Fig. 1. The solubility product relationship shown in equation (XI) is complicated at the lower pH values by the presence of H_2PO_4' ions. However, at pH value of 7.5 only about 14% of the total phosphate is present as H_2PO_4' ions and at a pH value of 8.5, the fraction is only about 1.4%. The concentration of this ion is, therefore, small and does not invalidate the reasoning outlined above.

In inhibitors capable of forming hydrated oxide products of reaction with ferrous ions, the passive potential decreases with increasing pH (Fig. 1), the opposite trend observed in phosphate solutions. In this case, however, the first step in the formation of hydrated-oxide corrosion product, usually lepidocrocite γ-Fe·O·OH (10), is probably the precipitation of ferrous hydroxide

$$Fe^{++} + 2OH' = Fe(OH)_2 \qquad \text{(XII)}$$

Although the exact mechanism of formation of lepidocrocite is not known, Schikorr (19) has suggested that it is formed by the slow oxidation of ferrous hydroxide by air, probably according to a reaction such as:

$$4Fe(OH)_2 + O_2 = 4FeO\cdot OH + 2H_2O \quad (XIII)$$

The over-all reaction may be written as follows

$$4Fe^{++} + 8OH' + O_2 = 4FeO\cdot OH + 2H_2O \quad (XIV)$$

It was suggested above that the rate of corrosion of iron at discontinuities in the passivity film decreased with increasing *p*H of the bulk solution. However,

$$S_{FeO\cdot OH} = K[Fe^{++}][OH]^2[O_2]^{1/4} \quad (XV)$$

and per unit increase in *p*H, $[OH']^2$ increases by a factor of 100. This large increase should easily outweigh the decrease in the rate of dissolution of the iron with increasing *p*H. The solubility product of lepidocrocite should, therefore, be exceeded more rapidly at higher *p*H values and the size of the inclusions of corrosion product should increase. Consequently the resistance of the pores, and also the value of the passive potential, should decrease with increasing *p*H of the inhibitor solution (Fig. 1). It is interesting to note that inclusions of lepidocrocite found in passivity films formed in sodium hydroxide were quite large, being of the order of 1–2 microns in diameter (5). Electron microscopic examination of films formed in sodium borate solution which has a much lower *p*H did not yield as clear cut results (10). Well-defined rings characteristic of γ-Fe_2O_3 were observed together with a few weak spots which might indicate the presence of a very small amount of second phase. This observation would be in accord with the reasoning outlined above although Mayne (20, 21) considers it possible that ferrous hydroxide can oxidize directly to γ-Fe_2O_3 or to magnetite, and that the presence of these compounds in passivity films does not necessarily imply that the film is formed by direct interaction of dissolved oxygen with the iron surface. However, the balance of the electron diffraction/electron microscope evidence supports the view outlined above.

The one exception to this behavior is that of sodium silicate solutions in which iron exhibits anomalously low values of passive potential (Fig. 1). Sodium silicate is believed to contain negatively charged colloidal silica particles (22) and these would be expected to be attracted to the anodic areas even before precipitation of corrosion product occurs. This would result in interference with the lateral growth of the oxide and would thus yield larger anodic areas of lower resistance and thus low values of the passive potential.

When solutions of sodium chromate, sodium nitrite, and sodium acetate were diluted, the steady-state value of the passive potential invariably became more noble. Similar behavior was observed on all inhibitors used in this investigation. The relationship between passive potential and inhibitor concentration is shown in Fig. 2. It is believed that the increase in passive potential accompanying the dilution of these inhibitors is due to (*a*) a decrease in *p*H of the solution, and (*b*) a possible small increase in oxygen concentration of the solution.

The first factor, which has been observed experimentally to be sufficient to account for the greater portion of the change in potential, increases the potential according to the reasoning outlined previously. The second factor, oxygen concentration, is important since it affects the rate of formation of the oxide film. At higher oxygen contents the rate of film growth, and hence the rate of lateral extension of the oxide, would be faster. If the corrosion rate of the iron at the anodic areas were essentially unchanged, then the final size of the inclusions of corrosion product would be smaller and the value of the potential higher. This point is considered in more detail later.

Potentials in phosphate solutions also become more noble with increasing dilution. Although the reduction in *p*H accompanying dilution would tend to shift the potential in the less noble direction (Fig. 1), dilution also decreases the concentration of $[HPO_4^{=}]$ ions which has a major effect on the solubility product of ferric phosphate (equation XI). Since the effect of *p*H on passive potentials in phosphate solutions is relatively small (Fig. 1), the effect of decreasing the $[HPO_4^{=}]$ ion concentration is more important. Thus, at lower concentrations of $[HPO_4^{=}]$ ions, more ferrous ions must pass into solution to exceed the solubility product of ferric phosphate. Consequently, a large period of time elapses before precipitation, dimensions of anodic areas decrease, and the passive potential becomes more noble.

Since it is believed that the final size of the inclusions of corrosion products determines the values of the passive potentials, it would appear likely that these potentials would be affected by surface pretreatment of the iron. Preparation involving immersion in hydrochloric acid results in a surface carrying less oxide than one that has been abraded with fine emery paper. Of course, the intervening brief exposure to air results in the formation of some oxide, but the areas available for initial anodic reaction should be larger on the acid-washed speci-

mens. Fig. 3 shows that the largest effect of surface pretreatment is observed at the highest *p*H values. It was suggested earlier that precipitation at discontinuities in the passivity film took place quickly in sodium hydroxide solution. In this solution, the oxide film has only a short period in which it can extend laterally. Consequently, it would be expected that, in this solution, the final size of the anodic areas should be quite highly dependent on the magnitude of their initial size. As the *p*H of the solution decreases it has been indicated that the time required for precipitation increases and so the effect of initial size of the anodic areas should decrease with decreasing *p*H.

The effect of the addition of 10 ppm of chloride ion to sodium benzoate, sodium hydroxide, and disodium phosphate solutions is more pronounced at high *p*H values than at low *p*H values (Fig. 4), and irregular form of the potential-time curves in sodium hydroxide and disodium phosphate suggests an alternate process of film breakdown and repair. Previous work (23) has shown that the addition of small amounts of chloride greatly reduces the internal resistance of corrosion cells, and that a large part of this reduction of internal resistance was due to the relative ease with which chloride ions can migrate through hydrated oxide corrosion products (23). Thus, at *p*H values where precipitation occurs earliest, the effect of chloride in reducing anodic polarization might be expected to be greatest (Fig. 4).

In sodium benzoate solutions the potential in the presence of chloride is steady and some 15 mv more positive than in the absence of chloride. This is probably due to a decrease of 0.15 *p*H units on addition of the chloride. The absence of fluctuation in potential of iron in sodium benzoate-potassium chloride solution is surprising and is not at present understood.

Fig. 5 demonstrates that, as the ease of access of air to the solution is increased, the value of the passive potential becomes more noble. Similar results have been obtained by Uhlig and Geary (3) using different oxygen concentrations. As the access of air, hence the oxygen concentration in solution, is increased, the rate of formation of γ-Fe_2O_3 and, consequently, its rate of lateral growth, should increase. If the rate of the corrosion process at discontinuities in the oxide film is not markedly changed, the size of the corrosion product inclusions should progressively decrease with increasing oxygen concentration. Accordingly, with increasing oxygen concentration, the anodic polarization and thus the value of the passive potential should increase as shown in Fig. 5. In the absence of oxygen the iron is no longer passive and the potential is of the order of -0.7 v (5).

Actually, the concentration of oxygen influences the solubility product relationships shown in equations (XI) and (XV) in the opposite direction to that considered above. However, oxygen concentration only enters these equations as the $\frac{1}{4}$ power and so its effect is comparatively small.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 Journal.

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Transformer Oil: Properties of Naphthenic and Aromatic Fractions[1]

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ABSTRACT

Transformer oil can be separated into naphthenic and aromatic fractions by percolation through silica gel. The following properties of the fractions have been determined: d-c conductivity, viscosity, viscosity index, interfacial tension, acid number, steam emulsion number, refractive dispersion, and molecular type. The behavior of these fractions in an arc is discussed with reference to the formation of gases, the production of carbon, and the structural changes of the molecules of the fractions.

Introduction

One of the more useful techniques for studying the constitution of petroleum-derived materials is selective adsorption. Based on the principles discovered by Tswett, the method is generally known as "chromatography." A technique developed by Mair and coworkers (1), called "displacement development," is particularly useful for the study of electrical insulating oil, the so-called transformer oil.

When a charge of transformer oil is allowed to flow into a column packed with silica gel, adsorption occurs. If the oil is then displaced from the column by a solvent more strongly adsorbed than any of the oil components, the displaced material is found to be separated into two principal groups. Normally, a water soluble alcohol is used for displacement. This permits extraction of the solvent with water. The raffinate oil is readily dried.

The two principal groups of components obtained from transformer oil differ greatly. The first group obtained is a water-white oil which appears to have no unsaturated carbon-carbon linkages. It has a relatively flat viscosity-temperature curve and a low pour point. This is called the naphthenic portion.

Following the naphthenic portion, a yellow oil is obtained. This oil shows characteristic reactions of aromatic compounds, has a steep viscosity-temperature curve, and may contain small quantities of oxygen, nitrogen, and sulfur. This oil is called the aromatic portion.

The types of hydrocarbon molecules normally occurring in petroleum fall into three major classes: paraffinic, naphthenic, and aromatic. The paraffins and naphthenes are concentrated together by the displacement development technique. The transformer oil used in this work did not appear to contain any paraffins. This was expected from the properties of the base-stock crude and the refining techniques used.

The distinction between an aromatic and a naphthenic molecule is rather precise: if the molecule contains an aromatic ring, it is classified as aromatic regardless of the other structures present. Compounds containing only cycloalkyl rings are known as naphthenes (2).

The available evidence about hydrocarbon types above the gasoline range in petroleum does not permit accurate location of side chains on either aromatic or naphthenic rings. There is good evidence, however, that when more than one ring is present in a compound, it is present in a fused ring system. The typical ring structures are Kata-condensed, rather than peri-condensed, or isolated (2). Strong evidence has been advanced to indicate that aromatic rings usually occur fused with naphthenic rings (3, 4). Structures having isolated rings may also occur (5), although more evidence is needed. For simplicity, only six-membered rings are used in these representations, although cyclopentyl rings may be present (2).[3]

The behavior of various molecular types when subjected to high voltage discharge (6), cathode rays (7), and capacitance sparks (8) indicates that naphthenic molecules produce large amounts of gas compared to aromatics, and that aromatics tend to have an inhibiting effect on gas production. Work on insulating oils (cable oils) under high voltage discharges (9) and arcs (10, 11) indicates that a similar trend might occur. The situation is complicated, however, by the effect of interrupter design (12). The aromatics also seem to promote forma-

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[3] A more thorough discussion of molecular structure may be found in reference (2), particularly pages XX and 94.

tion of carbon or "coke" (6, 9, 10). There is little data on the type of gas produced by the various molecular types upon arcing.

Aromatic types have higher viscosities and a lower viscosity index than naphthenic types of similar molecular weight. From the structure, one would expect aromatics, which are more polar molecules, to have a higher density, refractive dispersion, conductivity, and lower interfacial tension (against water); aromatics would be adsorbed more strongly than naphthenes on silica gel (2).

Experimental

Preparation of concentrates.—Twenty liters of uninhibited transformer oil were taken from a newly received tank car. This material was stored at room temperature in a sealed, opaque container. A Pyrex column 5 x 120 cm, packed with silica gel (Davison #922), was charged with 500 ml of transformer oil. A layer (2–4 cm) of silica gel was added on top of the column and reagent grade methanol was added from a reservoir under pressure (ca. ¾ kg/cm²). Effluent oils were collected, freed of methanol by washing with distilled water, dried, and stored in sealed glass containers. Approximately 10 l of oil were fractionated in this manner. The oil had a final yield of 82.5% (volume) naphthenic molecules. The losses in the column and due to subsequent manipulations were ca. 10% of the original volume.

Conductivity measurements.—Conductivity was measured using a calibrated cell of cylindrical shape. The cell was approximately 9 x 10 cm and had an electrode spacing of approximately 0.75 cm. The cell constant was 9.73 x 10^{-3} cm^{-1}.

Interfacial tension.—The procedure followed AS TM D971-50.

Viscosity and viscosity index.—The procedure followed ASTM D445-53 and D567-53.

Steam emulsion number.—The procedure followed ASTM D157-52.

Total acid number.—The procedure followed ASTM D664-49.

Physical properties.—Density, refractive index, refractive dispersion, and carbon content were measured as described previously (13).

Arcing tests.—A plexiglas test cup was used in the arcing tests. It was cylindrical, 4.5 cm I.D. and 14 cm high, and contained tellurium copper contacts which were arranged to give a variable gap space, fixed at 0.25 cm for this work. A 0.038 mm diameter michrome fuse wire bridged the gap. Application of load melts the fuse and arcing proceeds until the circuit is broken by a manually controlled oil switch. The load was applied from a 4.8 kv source, with a potential transformer of 2875:110 ratio connected across the gap, and a current transformer of 50:5 ratio in series with the gap. A magnetic oscillograph containing voltage, current, and watt elements was used to record the conditions of each run.

The 220 ml test cup was fitted with a cover sealed by a neoprene gasket, and clamped down. An opening in the side of the cup below the contact level was connected to a standpipe to permit escape of oil as the gases were formed by the arc.

From the calibration data, the arc energy in kilowatt seconds could be determined by planimeter integration of the oscillograph record. The procedure eliminates the necessity of accurate measurement of the effective arc column length; it also simplifies the adjustment of the contact gap, because only a low order of accuracy is necessary.

Molecular type analysis.—The molecular structures of the concentrates were determined by correlations with physical properties. The naphthenes were analyzed using the *n-d-M* correlations described by Van Nes and Van Westen (2), and the aromatics by the Hazelwood method (14). These correlations express the composition of an oil in terms of the average number of aromatic rings, R_A, and the average number of naphthenic rings, R_N, per molecule. These correlations can also be used to express the average number of paraffinic carbon atoms present as side chains on the ring, C_P (14).

Results and Discussion

Fig. 1 is a plot of current density vs. field intensity for the naphthenic and aromatic concentrates. Fig. 2 is a plot of conductivity vs. time for the concentrates, at a field strength of 20 kv/cm. These curves are similar to those obtained for hydrocarbons (15).

Table I summarizes the results of all the other tests on the aromatic and naphthenic concentrates. The polar nature of the aromatic concentrate is

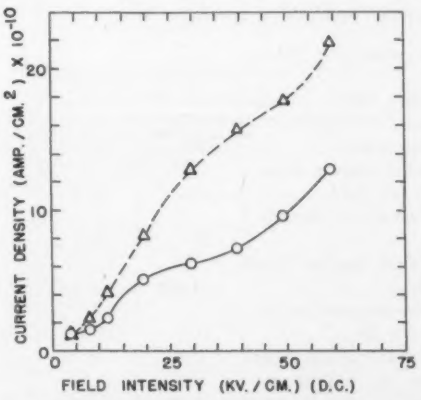


Fig. 1. Current density vs. field intensity d-c measurement. —○— Naphthenic concentrate; – –△– – aromatic concentrate.

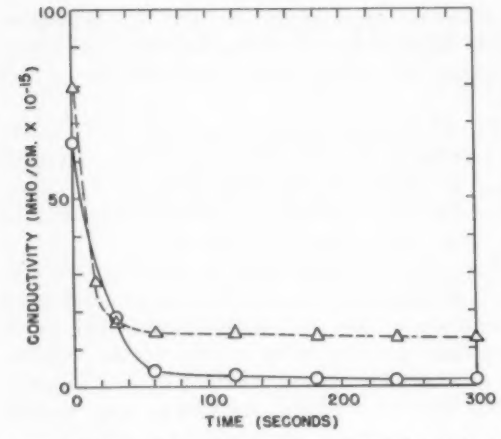


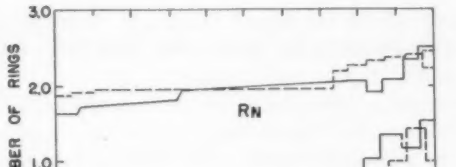
FIG. 2. D-C conductivity vs. time. Potential 20 kv/cm. —○— Naphthenic concentrate; - -△- - aromatic concentrate.

evident from the values of interfacial tension, conductivity, and refractive dispersion.

When a mixture of compounds, such as oil, is percolated through silica gel, fractionation occurs. The least polar compounds, being least strongly held by the adsorbent, move at the greatest rate and are eluted first. In the case of the transformer oil used in this work, the first compounds eluted are the naphthenes with the longest side chains. The aromatics follow the various naphthenes and, as a rule, the aromatics are separated on the basis of the number of aromatic rings present. Thus, the benzene type aromatic systems precede the naphthalene types, etc. Finally, after the aromatics, the oxygenated compounds, and the sulfur and nitrogen compounds, if any, are eluted (2).

TABLE I. *Properties of isolated oil concentrates*

	Naphthenes	Aromatics	Typical values for original oil
D.C. Conductivity (mho/cm)	1.9×10^{-15}	1.2×10^{-14}	—
Viscosity 100°F (centistokes)	7.96	11.32	9.3
Viscosity index	84	7.5	60
Interfacial tension (dyne cm^{-1}) (vs. H_2O)	45.2	29.2	44
Steam emulsion number (sec)	29	50	30
Total acid number (mg KOH/g)	0.003	0.018	0.010
Refractive dispersion $(n_F - n_C) \times 10^4$	77	127	83
Number of aromatic rings	0.00	0.93	0.40
Number of naphthenic rings	1.92	1.19	1.75
Number of paraffinic carbon atoms	9.2	7.7	8.8



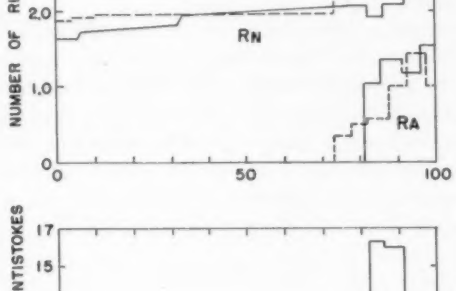


FIG. 3. Fractionation of transformer oil on silica gel. - - -Original oil; ——oil after arcing 60 times at 7.2 kv, 490 amp, 30% p.f. [See Reference (13)].

Fig. 3 shows percolation curves for a transformer oil before and after arcing in an oil circuit recloser (13). Table II lists the properties of the aromatics concentrated from these samples. The method of determining ring content, aromatic content, and number of paraffinic carbon atoms is based on that of Kurtz and Martin (16). The data indicate that there is a shift toward a higher molecular weight, a decrease in the amount of aromatic compounds present, and an increase in the number of paraffinic carbons. This agrees with the idea that the lighter fractions of the oil are decomposed, and that some aromatic rings are hydrogenated. Such fractionations, however, do not give conclusive information about processes involved in arcing.

Various studies on arcing in oil indicate that the primary reaction is to break down the oil molecules to hydrogen and hydrocarbon gases. Some carbon is formed as well. This carbon may be elemental carbon or highly cross-linked hydrocarbon polymers. The gases formed are approximately 70% hydrogen, 10–25% acetylene, and smaller amounts of methane, ethylene, and aromatics (11, 17, 18). The volume of

TABLE II. *Aromatic concentrate from original and arced oil*

	Before arcing	After arcing
Vol. % aromatics	17.5%	16.5%
Mol. weight	270	285
No. aromatic rings	1.16	1.18
No. naphthenic rings	1.35	1.30
No. paraffinic carbon atoms	7.5	8.6

gas produced per kilowatt second of arc energy is estimated to range from 35 cc (12) to 70 cc (11) for plain break contacts. Investigations of pure compounds indicate that naphthenes are somewhat decomposed, but that some fraction is converted to olefins and polymerized (6). Paraffins seem to be more susceptible to polymerization, and aromatics are readily condensed (6). In oil, some lighter fractions may be formed (17), and these are thought to promote gas formation (9).

Aromatic content of oils seems to be related to carbon formation (9). Condensation of aromatics could promote this (6), and the type of refining, which is related to the aromatic type, has an influence (10). Oura (19) showed that arcing produced approximately one-half as much carbon in a so-called "over-refined" transformer oil as in a normally processed oil.

This work did not demonstrate any marked difference in the volume of gas produced per kilowatt second in the naphthenic and aromatic concentrates (Fig. 4). The gas volume produced by the aromatic concentrate was only slightly less than that produced by the naphthenic concentrate. The difference, on only three samples, was not significant. The average for all samples is 55 cc gas/kw sec at S.T.P., in good agreement with other work. Kesselring (20) found 60 cc/kw sec, Magrini (21) found 53 cc/kw sec, Schrottke (22) found 56 cc/kw sec, and Muller (23) found 60 cc/kw sec. Todd and Thompson (12) suggest 60 cc/kw sec as reasonable for high currents, i.e., above 400 amp. In Fig. 5, which is a portion of an oscillograph tracing of arcing in the naphthenic concentrate, the arc current is 27 amp (rms). For low currents, Todd and Thompson (12) suggest a value of 35 cc/kw sec.

The oscillograph record shown in Fig. 5 is typical of runs on both naphthenic and aromatic concentrates. The upper trace is the arc watts. Periodic

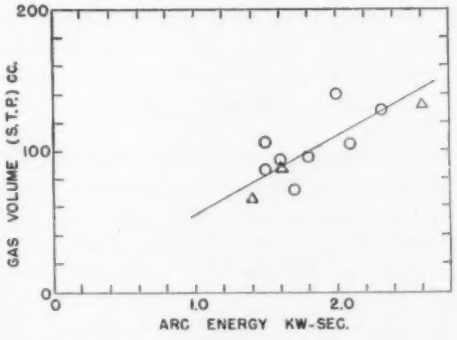


FIG. 4. Gas volume at S.T.P. vs. arc energy in kw-sec. ○ = Naphthenic concentrate; △ = aromatic concentrate. Average = 55 cc gas/kw sec; average deviation = 7.2 cc/kw sec; maximum deviation = 15 cc/kw-sec; standard deviation = 9.4 cc/kw sec.

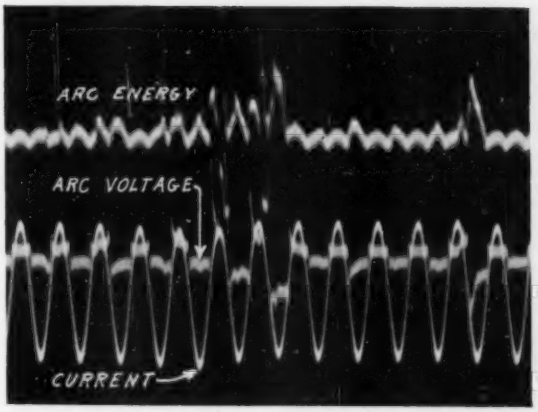


FIG. 5. Portion of oscillograph record of arcing in naphthenic concentrate.

bursts of energy were found in all cases. The sine curve is the current, and the other lower curve is the instantaneous arc voltage.

Fig. 6 is a diagram of the variations in the carbon contents of the samples. While there is a wide range of values, it appears that the aromatic concentrate generally produces much more carbon for a given amount of energy than the naphthenic concentrate. The aromatic concentrate averages approximately three times as much carbon per kilowatt second, in agreement with earlier work.

Oil samples from the various tests were filtered to remove the carbon. Refractive index, dispersion, density, and viscosities at 37.8°C (100°F) and 98.9°C (210°F) were determined. Molecular weight was calculated from the viscosity data (24). The percentage of aromatic *molecules* present (as opposed to the aromatic *rings*) was estimated from specific dispersion measurements (25).

Table III shows some of the results from selected runs. With the naphthenic concentrate, the percentage of aromatic molecules present increased.

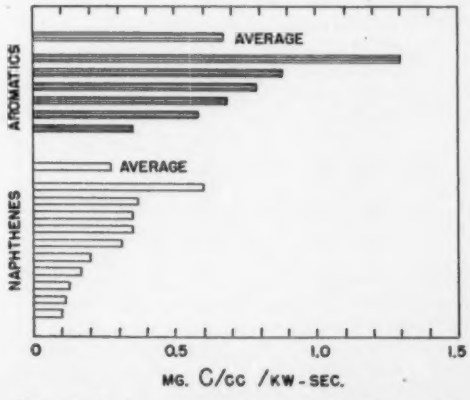


FIG. 6. Carbon content/kw sec for all samples

TABLE III. *Arcing tests of naphthenic and aromatic concentrates*

Material	M	V.I.	R_N	$\#C_P$	$AR\%$	Arc energy
Original naphthenic..	267	84	1.92	9.2	0.0	—
Naphthenic #1.....	274	86	1.97	9.5	3.3	5.4
Naphthenic #11.....	261	74	1.90	8.9	4.3	8.1
Original aromatic....	253	7.5	1.19	7.7	85	—
Aromatic #10.....	270	46	1.23	8.7	85	1.4

M = molecular weight calculated from two viscosities.
V.I. = viscosity index.
R_N = number of naphthenic rings.
$\#C_P$ = number of paraffinic carbon atoms.
$\%AR$ = percentage aromatic molecules, estimated from specific dispersions.
Arc energy = kw sec.

The general behavior was a decrease in molecular weight, viscosity index, and number of paraffinic carbon atoms. A very few cases, however, showed a pattern such as naphthenic run No. 1 in Table III.

The aromatics showed an increase in molecular weight, viscosity index, and number of paraffinic carbon atoms, and no change in the per cent of aromatic molecules present. There was evidence that the gases formed by arcing the aromatics contained considerably more acetylene than the gases from the naphthenes. Complete data are not available on this matter.

In a previous discussion of the mechanisms of arcing breakdown in transformer oil (13), the analogy to thermal cracking was cited. With the evidence obtained from work on the aromatic and naphthenic concentrates, this analogy becomes clearer. In thermal cracking, naphthenes tend to dehydrogenate their rings rather than to open them (26). Thus, in Fig. 7, reaction I is more probable than reaction II. In this figure, the nature and orientation of the alkyl side chains is not specified. There is some evidence to support a concept of a number of short side chains rather than one long side chain (2, 27). While the ring system is shown as a decalin ring, there are undoubtedly some compounds present with one or three naphthene rings as well. The decalin ring represents an average composition of the concentrate.

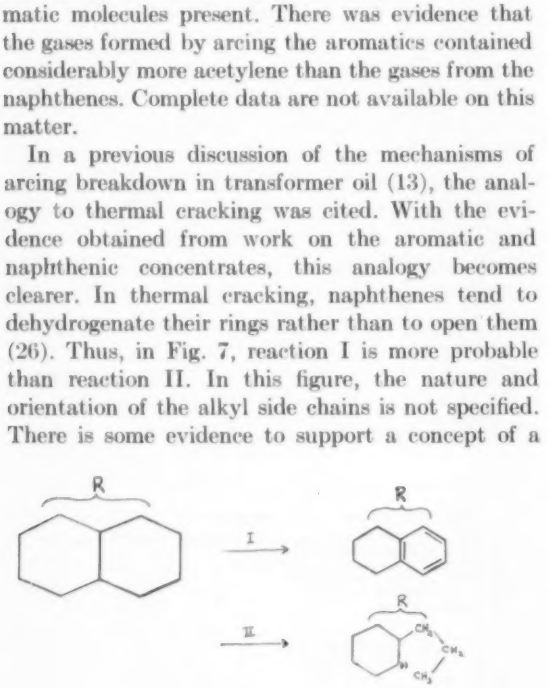


FIG. 7. Reactions of naphthenic molecules in an arc

Thermal cracking of naphthenes also causes a random splitting of side chains (26); this is represented by reaction III of Fig. 7. Finally, some decomposition to the elements and to light hydrocarbon gases occurs (reaction IV of Fig. 7). A further possibility is polymerization of the naphthenes (not shown).

If all of the reactions suggested are of equal probability, one could expect the mixture to have a lower molecular weight, an increase in aromatic content, a smaller number of paraffinic carbon atoms, and a lower viscosity index. If the polymerization reaction and selective decomposition of the lower molecular weight compounds occurs, there should be a shift toward higher molecular weight, increased naphthenic rings, higher viscosity index, and increased number of paraffinic carbon atoms. Forma-

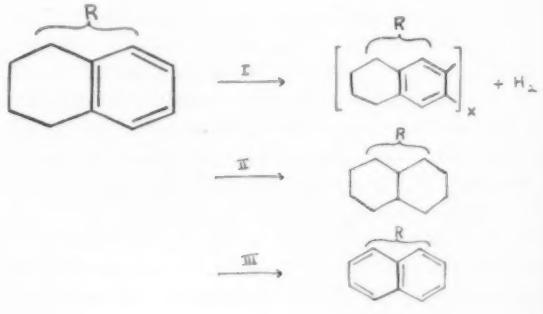


FIG. 8. Reactions of aromatic molecules in an arc

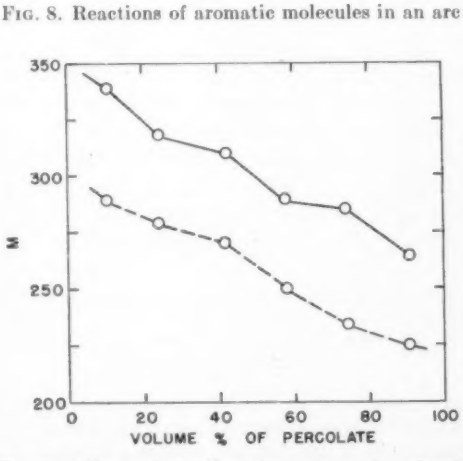


FIG. 9. Silica gel fractionation of arced and original aromatic concentrates. – – –Original; ——arced.

tion of aromatic rings should also occur. The authors have not been able to find good evidence for such a selective reaction pattern.

Fig. 8 shows some of the probable cracking reactions of the aromatic concentrate. An important feature of thermal cracking of aromatics is condensation of nuclei by elimination of hydrogen (26) (reaction I). This is similar to results found with high voltage discharges on pure aromatic compounds (6). Fig. 9 shows the results of silica gel fractionation of an aromatic concentrate before and after arcing. It can be seen that an appreciable number of higher molecular weight condensation products have been formed.

Further possibilities are hydrogenation of rings to naphthenic structures (reaction II), dehydrogenation of naphthenic rings to condensed aromatic systems like naphthalene (reaction III), and decomposition (IV). Reactions I, II, and IV of Fig. 8 are considered to be the predominant ones. It is unlikely that an appreciable quantity of aromatic rings is formed. The experimental data in Table III indicate that a significant increase in paraffinic carbons occurs, as well as an increase in naphthenic rings which might be significant. These would account for the increased viscosity index (2). It is possible that ring-opening is also a factor in the reactions.

The reactions of the molecular types can be summarized:

(*A*) The principal reaction caused by arcing of either molecular type in oil is decomposition to hydrogen, carbon and coke, and light hydrocarbon gases. Evidence presented indicates that the amount of gas produced is approximately the same for either molecular type for a given amount of arc energy; that the composition of the gases from naphthenic types and aromatic types may differ; and that aromatic types produce approximately three times as much carbon for a given amount of arc energy as do naphthenes.

(*B*) Secondary reactions of naphthenes yield aromatic molecules, and often involve a decrease in molecular weight as well as a decrease in side chain length. Little ring opening or condensation is involved.

(*C*) Secondary reactions of aromatic molecules yield condensation products by elimination of hydrogen and show side chain cleavage. A general shift to a higher molecular weight occurs, indicating the importance of condensation reactions.

Acknowledgments

The authors wish to thank Dr. C. M. Cheng and Mr. R. E. Riebs for their help in devising the arcing apparatus and tests, and for their help in performing the arcing experiments. Thanks are also extended to Mr. L. R. Larson for assistance in making the conductivity measurements and to Messrs. A. Van Ryan, L. A. Peppey, and L. C. Westphal for helpful discussions.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 Journal.

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Relation of Color to Certain Characteristics of Anodic Tantalum Films[1]

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ABSTRACT

Anodic oxidations of tantalum have been conducted over a range of formation voltages and temperatures. The thickness of the resultant film has been measured by several methods and related to the capacitance per unit area. The product of the voltage of formation, E, and the temperature of formation, T, (in °K) was found to be a constant for a specific film thickness. The gravimetric method of measuring film thickness was used to estimate a density lower than 8.7 commonly used for Ta_2O_5. Electrical losses of the Ta_2O_5 film are lower if the formation is carried out at higher temperatures. The color of the anodic film defines the voltage and temperature conditions of formation, which, in turn, determine the initial capacity and the expected capacity changes with time, temperature, and voltage stresses on accelerated life tests.

Introduction

The practical objective of this work was to produce an anodic film on tantalum which was as thin as possible and which resisted changes in thickness and electrical resistance under accelerated conditions of capacitor life test (usually rated d-c voltage at 85°C).

The studies were concerned with measuring film thicknesses obtained by known methods of anodic formation where formation voltage comprised the usual variable. The general procedure was to connect the tantalum to the positive terminal of a voltage supply and form to a given voltage at a given temperature. An estimate of film thickness was indirectly obtained by measuring the capacitance of the oxidized foil on a suitable capacitance bridge. The capacity in microfarads/in.^{2}, C, was known to vary inversely with the formation voltage, E. Since capacitance was also known to vary inversely with the thickness of the dielectric, then the thickness of the tantalum oxide varied directly with the formation voltage. Guntherschulze (1) shows that the thickness of a tantalum oxide film is 21 Å/v at 20°C. This statement, accurate as it may be, requires closer scrutiny, when formations are carried out not only at different voltages but different temperatures. It has been observed by the author that tantalum formed to a constant voltage at widely different temperatures varied greatly in capacity, inferring, therefore, wide differences in the film thickness. These suspicions were subsequently verified.

Four methods of measuring film thickness were selected. Two of these methods, namely, weight measurements and the use of the photoelectric spectrophotometer, have been reported also by Waber and coworkers (2) in their studies of the air oxidation of tantalum. The two other methods are a direct comparison with a standard color gauge, described by Blodgett (3) such as barium stearate interference colors, and the observance of maximum extinction points when examined with a sodium lamp.

Experimental Procedure

Tantalum of high purity, 10 mils in thickness, was rolled down in a Sendzimir mill to a thickness of ½ mil. Samples for anodizing were cleaned and thoroughly rinsed.

The sheet was then suspended in a forming electrolyte of the type commonly used and described by Deeley (4). Tantalum was connected to the positive terminal of the d-c power supply and a metal beaker served to complete the circuit. An on-off switch, a voltmeter, ammeter, and rheostat were also included in the circuit. The beaker may be heated with a Glas-col mantle or placed in a constant temperature bath. Temperature was kept to ±3°C. Anodizing for these experiments was performed at a current density of 20 ma/in.^{2} until terminal voltage was reached, after which constant voltage was applied for 1 hr.

After the oxide film was deposited, the tantalum sample was washed in distilled water, acetone dipped, and air dried prior to weighing or color comparison.

Specimens were anodized from 5 to 500 v and temperatures from 0° to 200°C. The capacitance, per cent dissipation factor, and electrical leakage

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measurements of the foil were made as a guide of expected performance in a capacitor. Some of these foils, or comparable ones, were used in a practical electrolytic capacitor and placed on accelerated life test. In addition to these tests, thickness measurements of the oxide film were made.

Gravimetric Results of Oxide Thickness

The procedure used to obtain the film thickness of anodized tantalum by the gravimetric method was to weigh the tantalum before and after anodizing on an analytical balance. The density of anodic Ta_2O_5 is assumed equal to that of the crystalline form. The oxide surface is assumed smooth and the area of the oxide assumed to be equal to the area of the tantalum sheet. When tantalum sheet deviates from smoothness, as it can be made to by suitable etching, then final results of thickness by this method will be in error by an order of magnitude equal to the etch ratio. The inherent roughness of tantalum is neglected in the nonetched sheets.

The thickness of the oxide film is calculated from the density, weight of film area, and formation voltage. The oxide film is assumed to be Ta_2O_5 as identified by x-ray diffraction techniques here. No other lines have been identified, although Waber and coworkers (2) in their studies of air oxidation of tantalum report that a phase other than Ta and Ta_2O_5 is present in oxidation products formed at 300°C and below.

Table I shows typical data obtained by the gravimetric procedure for 0.0005 in. tantalum which has been anodically oxidized to indicated voltage at 95°C. An estimated residual oxide thickness of 360 Å before formation if used as a blank would decrease the spread in results for T in respect to E.

Barium Stearate Step Gauge Results for Oxide Thickness

The step gauge reported by Blodgett (3) measures thickness of thin films by comparing the interference colors of the unknown film with the colors of the step gauge. Barium stearate film is constructed on special glass so that steps 2–16 μin. thick are shown (additional ranges are available). Each thickness reflects a characteristic color which is used as a standard.

TABLE I. *Gravimetric data for oxide thickness*

Sample area in cm² A	Formation voltage E	Weight change in grams W_1–W_2	Thickness in Å/v T
90.3	100	0.00545	19.7
90.3	200	0.01036	18.4
90.3	300	0.01498	17.7
90.3	400	0.01781	15.8
90.3	500	0.02122	15.0

Laws governing the interference of light rays reflected by thin films are fairly well established and detailed in standard texts in physical optics, and in Blodgett's report on the barium stearate step gauge. When light is reflected by a thin film of a transparent substance, part of the light is reflected at the upper boundary of the film and part at the lower boundary. Two rays may then travel together after reflection. Since one ray travels a longer distance they will, in general, have a phase difference as they emerge at the upper boundary. If the two rays are in phase, maximum intensity of light is reflected; if they are out of phase, less intensity is reflected. The intensity of the reflected light varies with film thickness. A plot of the intensity against film thickness results in a cosine curve. The "dark" series would correspond to the minima at thicknesses.

$\lambda/4n, 3\lambda/4n \cdots$ where n = refractive index of the film. The "bright" series would correspond to the minima at thicknesses $0, \lambda/2n, \lambda/n \cdots$

In the barium stearate step gauge, colors reflected by steps 2–8 are called the "first order" colors. Each of the first 3 orders starts with a yellow or yellow-brown, followed by dark blue, medium blue, etc.

Step 4 corresponds to the color of tantalum anodically oxidized at 20 v d.c. and 95°C for 1 hr. A 20 v, 95°C formation is then 4 μin. thick if the tantalum oxide refractive index were comparable to that of the barium stearate (1.491). While the refractive index for anodic Ta_2O_5 is not available, the geometric mean refractive index of the orthorhombic tantalum pentoxide and its optical dispersion can be represented by the Cauchy formula (2)

$$n = 2.033 + 8.74 \times \frac{10^6}{\lambda 2}$$

where n is the refractive index at λ wave length.

For sodium light of 5893 Å the refractive index of 2.275 can be used. This gives a calculated value of 2.62 μin. for the thickness of a 20 v film formed at 95°C or 33 Å/v. Step 12 of the barium stearate step gauge corresponds to the color of tantalum formed to 75 v d.c. at 95°C for 1 hr, or 27 Å/v. It would seem that similar to the gravimetric procedure there appears to be a blank which if taken into account would result in more constant value of Angstrom units per volt.

Maximum Extinction Results

Aside from the direct comparison with the step gauge, if a series of tantalum foils is formed from 5 v to 100 v d.c. for 1 hr at 95°C and then placed behind a source of sodium light, it will be observed that the 20 v film and the 75 v film are the darkest. Since they are, respectively, first and second order

minima, they may be calculated respectively $T_1 = \lambda/4n$ and $T_2 = 3\lambda/4n$: substituting the 5893 Å for the wave length of sodium light and the refractive index of 2.275 and dividing by the respective voltages, then 33 and 26 Å are obtained for thickness which compare favorably with step gauge results.

Recording Photoelectric Spectrophotometric Results

With a recording spectrophotometer measurements can be made of the color of reflecting materials such as the Ta_2O_5 interference colors. Any two colors that have the same spectrophotometric curve appear identical to the normal eye under any lighting conditions. In short, these color curves are the signatures of the different colors. The spectrophotometer used consists of a light source which radiates all wave lengths of the visible and near infrared spectrum, a monochromator for selecting monochromatic light as the spectrum, a monochromator for selecting monochromatic light as the spectrum is scanned, a flicker system for shining the light alternately on the sample and on a standard, a phototube and associated amplifier circuits, and a recorder. The monochromator is a double prism type which passes a constant wave-length band of 10 μ throughout the entire visible spectrum from 400 to 700 μ. Since the colors of the anodic Ta_2O_5 are a function of the oxide thickness, then a spectrophotometric curve could be used for the determination of thickness wholly independent of the human eye.

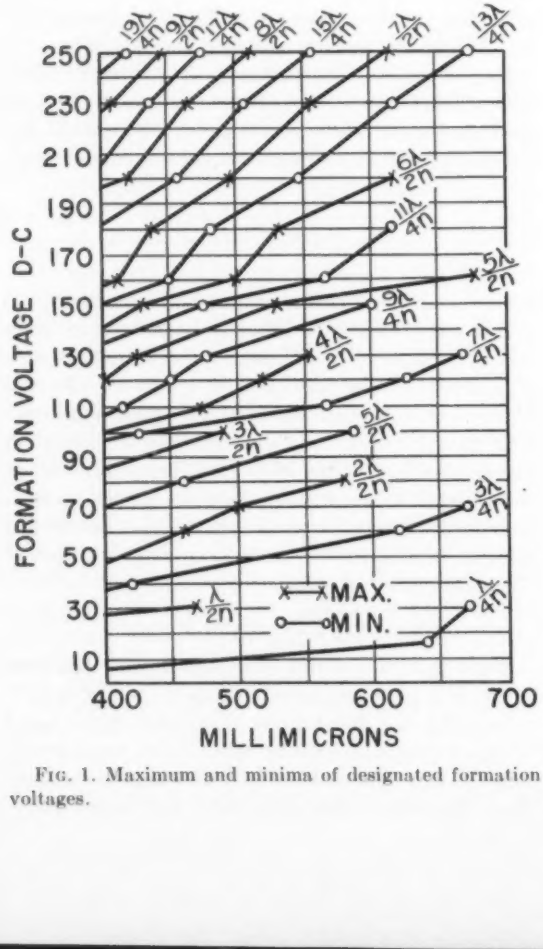

Fig. 1. Maximum and minima of designated formation voltages.

The minima and maxima points are easily read off the per cent reflectance vs. wave-length curve (4000–7000 Å). When a series of curves is plotted for anodized tantalum foils formed from very low voltage to high voltage, the minima and maxima points not only serve for thickness calculation but depict the order as well.

$$T \text{ minimum} = \lambda/4n, 3\lambda/4n, 5\lambda/4n \cdots$$

$$T \text{ maximum} = 0, \lambda/2n, \lambda/n, 3\lambda/2n$$

where T equals oxide thickness in Å for the first order, second order, etc., λ = wave length where minima or maxima occurs, and n = refractive index at corresponding wave length.

A plot of the minima and maxima points of a series of anodically oxidized foils vs. the formation voltage can be used to set up calibration curves (Fig. 1). By comparing the maxima and minima points of an unknown sample to the calibration curves, a good estimate of thickness and formation conditions can be obtained.

Comparison of Results Obtained

The three optical methods are considered in excellent agreement for this type of measurement and can be brought much closer by optical considerations of a phase shift in the wave length of light upon reflection from a metallic surface and the use of micro techniques. Considerations of surface oxide of the tantalum before anodizing have been recognized, but left uncorrected. Efforts to obtain a pattern by electron diffraction techniques of the tantalum metal before anodizing have been unsuccessful because of the rapid protective air oxide formation. An air-formed oxide is present on tantalum to a thickness of about 300 Å as determined by electron diffraction studies; this value may vary with the method of cleaning and the elapsed time between cleaning and anodizing.

The lower values of thickness obtained by the gravimetric procedure can be explained by postulating the presence of a gaseous constituent in the film. If enough oxygen were a part of the film structure to lower the density to 6.4, then the gravimetric results would agree with the optical data. The possibility also exists that the optical results have a constant error because of phase reversal considerations which have not been evaluated.

While it is not known by the author that the "gase-

TABLE II. *Film thickness of formed tantalum in Å/v at indicated temperatures*

Method of measurement	Temperature of formation			
	0°C	25°C	95°C	195°C
	Å	Å	Å	Å
Gravimetric results	13	16	20	25
Step gauge results	17	21	26	32
Spectrophotometric results	18	22	28	35

ous film" theory has been advanced for tantalum oxide films, it has been suggested by experimenters considering anodic aluminum oxide. Dieckmann (5) states that unused oxygen is driven into the pores of aluminum oxide film under high electrostatic pressure which tends to diffuse back into the electrolyte at increased temperatures and during shelf life.

Oxygen gas, which may be a part of the tantalum oxide film, would differ from aluminum in the direction of diffusion at increased temperatures. It is likely that there is a migration of oxygen at increased temperatures in the direction of the tantalum metal. The getter properties of tantalum and the less soluble oxide could account for the difference in behavior to that of the aluminum. Temperatures of several hundred degrees centigrade have been applied to anodically oxidized tantalum with no observed change in weight before and after air heat treating. However, a large increase in capacitance, leakage current, and per cent dissipation accompanies this treatment.

Table II summarizes the oxide thickness data by the various methods at various temperatures. Data nearest the 100 v anodic formation were arbitrarily selected as a compromise between the high results caused by "phase jumps" at the lower voltages and questionable uniformity of formation at higher voltages where "scintillation effects" can occur.

Electrolytic Cell Performance

If the data on oxide thickness are at least relatively correct, then it would be expected that a film formed on tantalum at 200 v and 95°C would have the same thickness as a film formed at 160 v and 195°C. It would be expected that a capacity reading in microfarads per square inch would be the same for the two formed foils although there is a 40 v difference in formation. This is exactly the case (Fig. 2). The same, of course, is true over a much wider range limited mainly by the proper choice of electrolytes to avoid dull films which are connected with dielectric breakdown, a specialized subject not discussed here.

When two tantalum sheets have been anodically formed to the same oxide thickness but at widely

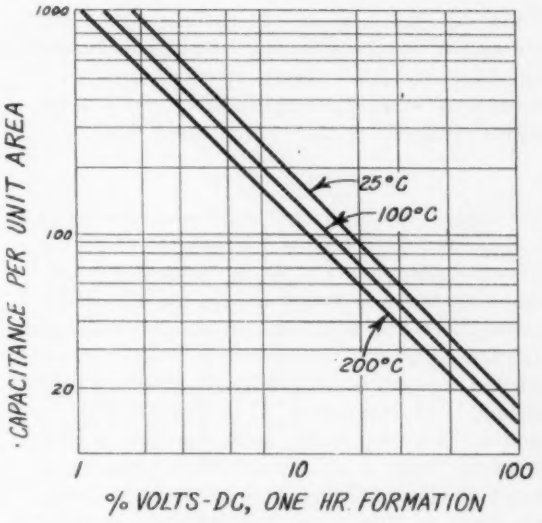

Fig. 2. Capacitance per unit area with voltage and temperature of formation of 0.0005 in. tantalum.

different temperatures and voltages, it has been observed that the sheet which has been anodized to the higher temperature exhibits lower electrical losses. The oxide film allows fewer electrons to penetrate to the tantalum metal, consequently the current flow is reduced. The author believes that in forming to a higher temperature more oxygen is driven into the film toward the tantalum metal underneath. This oxygen acts as a barrier and inhibits the current flow.

It is not the intent of the author to offer a mechanism for the formation of anodic tantalum oxide. Cabrera and Mott (6) have proposed a theory of the oxidation of metals where the metal ion is said to move through the metal oxide layer and combine with oxygen. Vermilyea (7) has supplemented this study and discussed the logarithmic growth law of Cabrera and Mott. In order to explain all of the results reported in this paper it would appear to the author that an additional effect of oxygen migration through the oxide film occurs at least under special conditions as well as the tantalum ion migration.

Summary

The anodic oxidation of tantalum from 0° to 200°C and up to several hundred volts d.c. has been studied by gravimetric, optical, and electrical measurements. The correlation of thickness results with voltage and temperature are reproducible and constant in trend. The higher temperature at fixed voltages produces a thicker anodic film which is additionally borne out by capacity measurements. The product of the forming voltage, E, and the absolute temperature, T, are a constant for a given capacitance per square inch so that $E_1T_1 = E_2T_2$.

The gravimetric procedure gives lower results and lends support to a lower density for anodic tantalum oxide films and an "oxygen film" theory. This gaseous layer is used to explain the lower leakage currents obtained on high temperature films.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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Chloride and Sulfate Ion Contamination of Zinc Sulfide Precipitates[1]

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ABSTRACT

Data are presented to show that zinc sulfide precipitated from chloride or sulfate solutions retains from 0.2 to over 2% chloride or sulfate ion after thorough washing. Ion displacement experiments show that sulfate contamination is mainly or entirely a surface phenomenon; results with chloride are not as conclusive; there seems to be both surface and volume contamination. The exchange is mainly anionic; only small quantities of zinc and hydrogen ions are displaced. Digestion of anion contaminated sulfides for periods up to 500 hr in water at 70°C removes only a fraction of the contaminating anions; for example, only 7% of chloride ion is removed after 212 hr, and 16% of the sulfate after 228 hr.

INTRODUCTION

Many investigations have been carried out on the physical properties, particularly luminescence, of zinc sulfide. In most cases scant attention has been paid to the purity of the material, and, in those instances where the investigators have been purity conscious, their interest has, with few exceptions, been restricted to contamination by heavy metals. Work and Odell (1), Rothschild (2), and Smith (3) indicate that precipitated zinc sulfide can be contaminated with the anion of the zinc salt used in the precipitation. Recent investigations in this laboratory have shown that all zinc sulfide derived via aqueous precipitation is contaminated with substantial quantities of sorbed water[3] (removable only at temperatures above 400°C), sulfate, and frequently chloride. Zinc sulfide which contains sulfate must be presumed on firing to become contaminated with zinc oxide (5). The fate of contaminating chloride on firing is not yet clear; after firing the quantity left behind may be undetectable by ordinary chemical means yet, before it is expelled, it may play a crucial role in the formation of luminescent centers. The contaminating chloride and sulfate cannot be ascribed to insufficient washing. Typical values for washed zinc sulfide[4] are: chloride, 0.72%; sulfate, 0.34%.

The occurrence of sulfate or chloride in the washed precipitate is due to precipitation of the zinc sulfide from zinc sulfate or zinc chloride solution, respectively. Generally, no matter what anion is present in the precipitating solution, one must expect that anion to be a contaminant of the zinc sulfide.

EXPERIMENTAL

The experimental procedures used to determine the nature of the anionic contamination of precipitated zinc sulfide were as follows:

A. Digestion experiments.—Precipitated zinc sulfide was digested in distilled water at 70°C and the amount of anionic contamination retained by the precipitate as a function of the time of digestion was determined.

B. Precipitation experiments.—Zinc sulfide was precipitated from mixtures of zinc chloride and zinc sulfate solutions and the washed[5] precipitate investigated for the amount of retained anions (chloride and sulfate).

C. Ion displacement experiments.—Contaminated precipitates were leached[5] with solutions of chloride or sulfate salts to replace, respectively, the original sulfate or chloride contaminant in washed zinc sulfide precipitates.

Samples of zinc sulfide were prepared from both zinc chloride and zinc sulfate solutions by precipitation with tank hydrogen sulfide. Two to three liters of 0.5M solution were adjusted to *p*H 2.5 at the start by addition of hydrochloric or sulfuric acid, respectively. The temperature of the solution was

[1] Manuscript received July 16, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

[2] Chemistry Department, Brooklyn College, Brooklyn, New York; Consultant, Physics Laboratories, Sylvania Electric Products Inc.

[3] Becker and Grassman (4) have shown that this bound water is not water of hydration.

[4] As evidenced by the absence of those anions in the washings.

[5] Washing refers to the treatment of a zinc sulfide precipitate with distilled water to remove contaminants; "leaching" to the treatment of the zinc sulfide with a salt solution (usually sodium chloride or sodium sulfate) to replace the original contaminant with a different species.

TABLE I. *Analyses of unfired, unactivated* ZnS

Sample No.* %	1	2	3	4	5	6	7	8
$SO_4^=$	2.65	0.56	0.73	0.34	0.46	0.41	1.81	1.90
Cl^-	0.98	0.53	0.82	0.72	0.00	0.00	0.00	0.00
NH_4^+	0.55	0.03	0.04	—	—	—	—	—
H_2O	0.81	1.08	1.43	—	—	—	—	—

* Numbers 1–6 are commercial samples; 7–8 are laboratory preparations.

70–75°C, and the hydrogen sulfide was maintained at a gauge pressure of 5 in. of water. The time of precipitation was from one to three hours. During precipitation the formation of hydrochloric or sulfuric acid caused the *p*H to drop; generally the final *p*H was 1.0 to 1.2.

Where precipitation was from mixtures of the chloride and sulfate, the mole ratio of chloride to sulfate was varied from 0.05 to 0.50 keeping the zinc molarity constant at 0.5M.

The precipitate obtained was filtered immediately, washed with distilled water at 70°C until three successive washings showed no chloride or sulfate, then dried at 110°C for 24 hr. Filtration was accomplished on fritted glass filters. Samples difficult to filter were centrifuged. The volume of wash water was approximately 10 milliliters per gram of solid per wash. The number of washings required before the filtrate was free of chloride and sulfate varied with the particular sample. Chloride precipitates were the most difficult to wash. Fifteen to twenty washes were usually required for precipitates from sulfate solutions.

1. Analysis for impurities in zinc sulfide.—Analytical data are presented on an oven dry (110°C) basis. For the determination of chloride and sulfate the procedure was to dissolve the sample in hot 4*N* nitric and hydrochloric acid, respectively, boil gently to expel all the hydrogen sulfide, and then neutralize with aqueous ammonia.[6] Chloride and sulfate were determined by standard gravimetric methods, the former as silver chloride, the latter as barium sulfate. Duplicate runs were made on each sample. Ammonium ion was determined by the Kjeldahl method. Analyses of commercial samples and those prepared at this laboratory are given in Table I.

2. Digestion of zinc sulfide.—Since thoroughly washed zinc sulfide contains substantial quantities of sulfate and/or chloride (see Table I), it was decided to determine whether these anionic impurities are retained (*a*) by coprecipitation, that is, by entrapment in the forming lattice during precipitation,

[6] The evolved gases were checked for entrained or volatile chlorides in several determinations. No chloride was found.

TABLE II. *Digestion of* ZnS, Cl^- *in* H_2O *at 70°C. (Initial* Cl^- *content = 0.72%)*

Hours	% Cl^- in solution	% Cl^- remaining in ZnS	Total
27	0.043	0.67	0.71
27	0.041	0.70	0.74
75	0.047	0.67	0.72
75	0.047	0.67	0.72
116	0.051	0.68	0.73
116	0.051	0.68	0.73
212	0.053	—	—
212	0.053	—	—

TABLE III. *Digestion of* ZnS, $SO_4^=$ *in* H_2O *at 70°C. (Initial sulfate content = 1.86%)*

Hours	% $SO_4^=$ in solution	% $SO_4^=$ remaining in ZnS	Total	Increase in $SO_4^=$
4	0.36	1.54	1.90	0.04
4	0.36	1.54	1.90	0.04
21	0.41	1.52	1.93	0.07
21	0.41	1.52	1.93	0.07
48	0.45	1.55	2.00	0.14
48	0.45	1.55	2.00	0.14
141	0.58	1.55	2.13	0.17
141	0.59	1.55	2.14	0.18
288	0.86	1.57	2.43	0.57
288	0.90	1.55	2.45	0.59
528	1.13	1.60	2.73	0.87
528	1.15	1.59	2.74	0.88

or (*b*) by adsorption. Two methods, digestion and ion displacement, were employed. The former method might liberate a portion of the contaminant if it were in the lattice; the latter method would be confined to the surface of the zinc sulfide crystallites.

Weighed samples of washed and dried zinc sulfide, prepared from chloride solutions, were digested with 200 milliliters of distilled water at 70°C for from 27 to 212 hr. During digestion the samples were stirred every four hours. After digestion the samples were filtered and washed, and the chloride content of the filtrate determined. Table II shows that there is a definite increase in the amount of chloride released

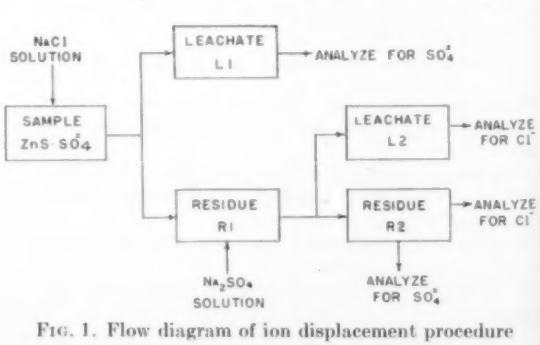

FIG. 1. Flow diagram of ion displacement procedure

TABLE IV. *Effect of ion displacement of* $SO_4^{=}$ *and* Cl^- *from* ZnS

Run	Sample, g	Initial sulfate		Displaced $SO_4^{=}$		% Displaced	Leached with
		%	g	g	meq/g		
1	10.267	0.31	0.0318	0.0204	0.0414	64.1	1*N* NaCl
	11.571	0.31	0.0359	0.0203	0.0365	56.5	
2	10.978	0.31	0.0340	0.0227	0.0431	66.8	2*N* NaCl
	7.869	0.31	0.0244	0.0186	0.0492	76.2	
3	5.133	1.99	0.1021	0.0950	0.386	93.0	2*N* NaCl
	5.145	1.99	0.1024	0.0957	0.388	93.5	
4	3.697	1.99	0.0736	0.0747	0.421	101.5	2*N* NaCl
	3.702	1.99	0.0737	0.0740	0.416	100.4	
5	4.544	1.82	0.0827	0.0668	0.306	80.8	2*N* K_2S
	4.365	1.82	0.0794	0.0637	0.304	80.2	
		Initial Chloride		Displaced Cl^-			
		%	g	g	meq/g		
6	4.504	2.32	0.1045	0.0195	0.122	18.7	2*N* $MgSO_4$
	4.502	2.32	0.1044	0.0196	0.123	18.8	
7	4.557	1.17	0.0533	0.00756	0.0468	14.2	2*N* Na_2SO_4
	4.919	1.17	0.0576	0.00807	0.0463	14.0	

TABLE V. *Effect of cyclical displacement of* Cl^- *and* $SO_4^{=}$ *on* ZnS

Run No.	Sample, g	Initial $SO_4^{=}$ meq/g	L_1, $SO_4^{=}$ removed meq/g	R_1, $SO_4^{=}$ remaining meq/g	L_2, Cl^- removed meq/g	R_2, Cl^- remaining meq/g	R_2, $SO_4^{=}$ remaining meq/g
1	3.697	0.415	0.421	0.00*	0.280	—	0.318
	3.702	0.415	0.416	0.00*	0.344	0.00	—
2	4.122	0.379	0.316	0.063*	0.0789	0.0034	—
	4.184	0.379	0.316	0.063*	0.0789	0.0034	—
3	10.978	0.0645	0.0431	0.0214*	—	—	0.0473
	7.869	0.0646	0.0492	0.0154*	—	—	0.0466
		Initial chloride meq/g	Cl^- removed meq/g	Cl^- remaining meq/g	$SO_4^{=}$ removed meq/g	$SO_4^{=}$ Remaining meq/g	Cl^- remaining meq/g
4	4.504	0.654	0.122	0.532*	0.0777	—	0.542
	4.502	0.655	0.123	0.532*	0.0717	—	0.539

* Calculated value = initial value − amount removed.

as the digestion becomes longer, but that the amount is small compared with the chloride remaining in the solid phase.

A similar experiment was performed with zinc sulfide prepared from sulfate solution. Results are presented in Table III, which shows that the sulfate content of the solid phase is relatively unchanged, while that of the solution increases. The enrichment in sulfate must be attributed to oxidation of zinc sulfide during digestion.

3. Ion displacement on zinc sulfide.—Freshly precipitated zinc sulfide has a large surface to volume ratio.[7] If part or all of the anionic contamination is due to adsorption, that contamination should be replaceable by leaching with a solution of a different anion. Accordingly, samples of zinc sulfide prepared from zinc sulfate solution were weighed and placed into fine fritted glass funnels and 25 milliliters of 1*N* or 2*N* sodium chloride (at 70°C) added. The solution and precipitate were left in contact, with stirring. After fifteen minutes the chloride solution was filtered off by applying vacuum and a fresh 25 milliliter portion added. The process was repeated until 300 milliliters had been contacted with the zinc sulfide. The leachings were analyzed for sulfate.

To determine whether displacement is reversible the samples, which had been leached with sodium chloride, were washed until the filtrate was chloride free, then leached with 1*N* or 2*N* sodium sulfate. The leachings were analyzed for chloride. Similarly, zinc sulfide samples with initial chloride contamination were leached first with 1*N* or 2*N* sodium sulfate at 70°C, then with water until the filtrate was sulfate free, and finally with 1*N* or 2*N* sodium chlo-

[7] Gas adsorption measurements and electron microscope examination show that precipitated zinc sulfide particles are 100 to 1000 Å in diameter.

TABLE VI. *Ion displacement on zinc sulfide with initial chloride and sulfate contamination*

Mole ratio $Cl^-/SO_4^=$ in precipitating solution	0.05	0.10	0.50
% Initial chloride in ZnS	0.89	1.15	1.47
% Initial sulfate in ZnS	1.49	1.58	1.39
% Initial chloride displaced by 2*N* Na_2SO_4	15.7 13.5	11.3 10.4	13.6 12.9
% Initial sulfate displaced by 2*N* NaCl	91.9 91.9	81.5 81.0	92.7 92.0

TABLE VII. *Cation and anion displacement in ZnS precipitated from sulfate solution*

Weight of sample g	Initial $SO_4^=$, meq.	Meq. removed by 2*N* KCl		
		Zn^{++}*	H^+	$SO_4^=$
1. 4.135	1.567	0.0896	0.060	1.317
2. 4.135	1.567	0.0784	0.048	1.291
3. 5.172	2.144	0.0841	0.044	1.923
4. 5.173	2.144	0.0841	0.052	1.923

* The observed Zn^{++} displacement is only slightly greater than the normal solubility of ZnS in water.

ride.[8] A flow diagram of the procedure is shown in Fig. 1; results are given in Tables IV and V.

With zinc sulfide samples prepared from mixed chloride and sulfate solutions, separate samples from each run were leached with 2*N* sodium chloride and 2*N* sodium sulfate at 70°C and the leachings analyzed for sulfate and chloride, respectively. Results are given in Table VI.

The results are summarized as follows.

1. With chloride-contaminated sulfides the displacement takes place to a considerably lesser extent than with sulfate-contaminated precipitates (Table V, columns 3 and 4). For sulfides contaminated with both chloride and sulfate the chloride is displaced to a considerably lesser extent than is the sulfate (Table VI).

2. When chloride displaces the sulfate of a sulfate-contaminated precipitate, the chloride can be removed by subsequent leaching with sodium sulfate solution (Table V, run 1, columns 6 and 7).

3. In all cases it was found that the displacement was nonstoichiometric, i.e., milliequivalents of sulfate removed from the precipitate were greater than the milliequivalents of chloride added to the precipitate.[9]

Ion displacement experiments were extended to determine whether appreciable cation exchange occurred. Samples of sulfate-contaminated precipitates were leached with 2*N* sodium chloride and 2*N* potassium chloride. The leachate was divided in half, zinc and hydrogen ions were determined in one half and sulfate in the other. Zinc was determined as the sulfide and hydrogen ion by titration with sodium hydroxide. The results are shown in Table VII. In all cases the sum of the milliequivalents of zinc and hydrogen ion was much less than the milliequivalents of sulfate exchanged.

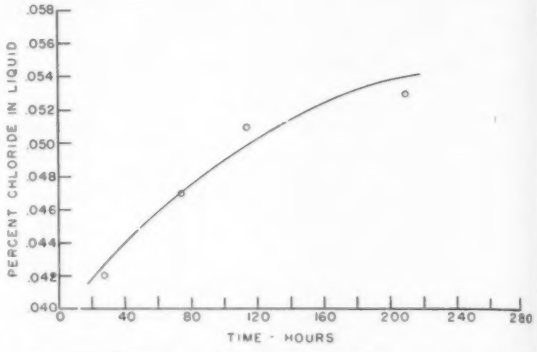

FIG. 2. Digestion of ZnS, Cl^- in H_2O at 70°C; initial Cl = 0.72%.

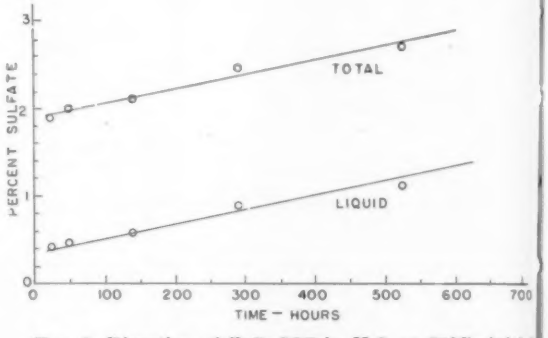

FIG. 3. Digestion of ZnS, $SO_4^=$ in H_2O at 70°C; initial $SO_4^=$ = 1.86%.

DISCUSSION

When zinc sulfide contaminated with chloride or sulfate is digested it is seen (Tables II and III, Fig. 2 and 3) that a small percentage of the contaminant is extracted. This release could conceivably be from the interior of crystallites by a process in which small crystallites dissolve in the aqueous digestion medium yielding zinc and sulfide ions and simultaneously precipitate on existing larger crystallites. In such a process the occluded contaminant released does not tend to become reoccluded because (*a*) its concentration in the solvent is now very small, and (*b*) the growing crystallite is adding zinc and sulfide ions under thermodynamically reversible conditions,

[8] Several runs were made using 2*N* potassium sulfide. These solutions were extremely difficult to filter through the zinc sulfide bed and their use was discontinued. A typical run using potassium sulfide is shown in Table IV.

[9] If a portion of the adsorption attributed to sulfate is actually bisulfate the number of milliequivalents of adsorbed ions is smaller. However, on the basis of the amount of titratable hydrogen displaced (Table VII), it appears that little bisulfate is present.

situation leading toward crystal perfection. The small quantity of contaminating anions released after long digestion, about 7% in the case of chloride and 16% in the case of sulfate, indicates that this solution process (i.e., the growth of large crystallites at the expense of the small ones) occurs to a limited extent, if at all.

The release of contaminant during digestion may be explained on the basis of a "regularization" of the precipitated crystallites. In the technique which the authors employed (and which is practically universally employed) the zinc sulfide is precipitated under thermodynamically irreversible conditions. Consequently the crystallites formed do not have a minimum surface energy, and are irregular (6). As the crystallites are permitted to digest they tend to minimize their surface energy by becoming more regular. If contaminating anions are held by surface forces, a decrease in the specific surface by the regularization of the crystallites will release them, and the amount of anions released will be roughly proportional to the decrease in surface. That this is the mechanism by which anions are released during digestion is indicated by the experiments involving ion displacement.

In the ion displacement experiments when sulfate-contaminated zinc sulfide was leached with sodium chloride solution 56% to 100% of the sulfate was readily displaced. Furthermore, as the ratio of mass of chloride to mass of zinc sulfide was increased, so was the percentage of sulfate displaced also increased. Since the leaching solution has access only to the surface, it must be presumed that the sulfate removed was situated on the surface. In the instance where complete sulfate removal was achieved by displacement with chloride, all the sulfate contaminating the zinc sulfide (1.99%) must have been on crystallite surfaces.

Concomitant with the anion exchange there occurs a small amount of cation exchange (Table VII). One would expect a material to show one or the other of these displacement phenomena, but not both. Under the conditions of precipitation, i.e., excess zinc (from zinc sulfate or zinc chloride), the zinc sulfide formed is positively charged and will adsorb negative ions (sulfate, chloride, etc.) from the solution to compensate for this excess charge.[10] These negative ions will be held loosely compared to the positive ions initially taken up by the zinc sulfide and are, therefore, easily displaced by a high concentration of a different anion. Experimental data support this hypothesis. In fact, in the case of the sulfate exchange, the ratio of milliequivalents of cation exchanged to milliequivalents of anion exchanged in the four experimental runs is less than 0.11.

[10] Kolthoff indicates that precipitated zinc sulfide is positively charged (7).

TABLE VIII. *Tetrahedral* and ionic radii in Å*

Atom	Tetrahedral radii	Ionic radii
Zn	1.31	0.74 (+2)
S	1.04†	1.84 (−2)
Cl	0.99	1.81 (−1)
O	0.66†	1.40 (−2)

* Derived from interatomic distances in crystals where the atoms form four tetrahedral bonds, e.g., ZnS.

† On this basis the tetrahedral $SO_4^{=}$ ion would have a radius sum of 1.70 Å. Observed values of the S-O distance are ~1.50 Å. The sphere circumscribing the $SO_4^{=}$ ion is, therefore, 1.50 + 0.66 = 2.16 Å. A substitution of $SO_4^{=}$ for $S^{=}$ corresponds to replacement by an ion 107% larger than the $S^{=}$, i.e.,

$$\frac{2.16 - 1.04}{1.04} \times 100 = 107\%$$

The results on the removal of chloride from zinc sulfide were different from those obtained in the case of sulfate. Leaching a sample of high chloride contamination with 300 ml of 2*N* sodium sulfate resulted in replacement of only 19% of the chloride; in other cases 14% was replaced.

The data (Table V, run 1) also show that chloride introduced on the surface of a zinc sulfide sample (by exchanging the original sulfate contamination with chloride) can be completely removed by subsequent washing with sodium sulfate solution. However, samples of zinc sulfide initially contaminated with chloride show that only a small fraction (ca. 10–19%) of the total chloride can be displaced.

Similar results obtain for sulfide samples with both initial chloride and sulfate contamination. Here a maximum of 15.7% of chloride could be displaced with 2*N* sodium sulfate. For the same sample 91.9% of the sulfate contamination was removed with 2*N* sodium chloride.

From comparison with the results of displacement with sulfate-contaminated precipitates, it is indicated that chloride exists both in the interior and on the surface of the zinc sulfide crystallites.

Table VIII lists the ionic radii and the tetrahedral "covalent" radii[11] of the atoms of interest in the preparation of ZnS from aqueous solutions containing the chloride and sulfate salts. On the assumption that zinc sulfide is covalent, substitution of chlorine for sulfur atom involves the exchange of atoms of comparable size. Replacement by sulfate, however, requires the substitution of an ion that is about 107% larger than the sulfur atom.[12] Similarly, if

[11] Derived from interatomic distances in crystals where the atoms form four tetrahedral bonds, e.g., ZnS (8).

[12] The sulfate ion is assumed to act as a sphere of radius equal to the observed S-O distance plus the radius of the O atom.

zinc sulfide is assumed to be an ionic crystal,[13] the replacement of sulfur by sulfate requires the exchange with an ion about 58% larger than sulfur. From considerations of ionic size alone it would appear that the formation of a solid solution of zinc sulfide and zinc chloride is possible, while a solid solution of zinc sulfide and zinc sulfate is not.

Acknowledgments

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[13] Born indicates that zinc sulfide is partly covalent (9).

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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Production of Zirconium Alloys by Consumable Electrode Arc Melting[1]

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ABSTRACT

The technique and advantages of consumable electrode arc melting and remelting in the production of zirconium alloys are discussed. Descriptions of the equipment and conditions of operation involved in double melting are given. Discussion of homogeneity, purity, and effective yield is included.

Introduction

Zirconium metal poses many special problems in melting operations because of its high melting point and its great chemical reactivity which prevents the use of known refractories and melting techniques (1). While several methods have been developed which are relatively successful in producing ingots of zirconium (and titanium), most of these cause considerable contamination. More serious immediate problems occur in the production of alloys where lack of homogeneity and rather high scrap loss are encountered. Consumable electrode arc melting is particularly effective in controlling these two problems, and makes possible the production of alloys more economically by greatly increasing the actual amount of metal available for effective use (2).

Experimental

The basic design of a furnace for experimental melting of consumable electrodes has been described (3) as has a production model of such a furnace (4). It is the alloy products of this type of furnace that are discussed. The furnace makes use of 2 in. x 2 in. x 20 in. electrodes pressed from zirconium sponge and operates under atmospheric pressure of an inert gas (see Fig. 1).

Electrodes (A) are placed in a guide clamp (B) by use of rubber gloves (C) sealed into the furnace wall. A small tungsten electrode welding arc (D) is used to join the electrode sections into the melting electrode which passes through steel drive rolls (E) and water-cooled copper rolls (F) which apply the melting current. The electrode is advanced until it strikes a pad of zirconium turnings in the bottom of the water-cooled copper melting cup (G) whereupon melting is initiated. Additional electrode sections are joined continuously to the top of the melting electrode until the desired ingot is melted. Additional features of the furnace are the alloy adding device (H) and the control field coil (J). This furnace was quite successful in turning out zirconium ingots of high quality.

Power for melting is produced by banks of standard dual 400 amp selenium welding rectifiers. These machines balance the load on the 3 phase 440 v main power line and provide very flexible and convenient energy for melting. They furnish 60% of their rated output continuously. Arc current stability is excellent in that voltage recovery requires only one-half cycle.

The pressed sponge electrodes employed are pressed at 50 tons/in.^{2} which gives them a density 87% that of metallic zirconium. The bars weigh 7.5 kg each and have an electrical resistivity of 1.6 x 10^2 microhms/cm^3. Breaking strength of the electrodes in tension for various conditions of pressing is as follows:

Pressure (tons/in.^{2})	10	20	30	40	50
Breaking strength, 2 in. x 2 in. bar (lb)	115	850	2200	2610	6900

A standard 2 in. x 2 in. pressed sponge electrode operates satisfactorily while carrying up to 5000 amp at 40 v in producing a 10 in. diameter ingot. As a 10 in. ingot is as large as is usually used for remelting purposes, tests beyond this point have not been made.

A few simple changes permit alloy ingots to be produced. Powder, shot, or wire of the appropriate alloying agent were added centrally in the sponge bar at the time of pressing. Several problems which resulted from the rigid specifications of the finished ingots are worthy of discussion.

Most commercial metal powders are relatively expensive and impure, (particularly in regard to oxygen and nitrogen contamination). An alternate choice is to produce a master alloy of some suitable

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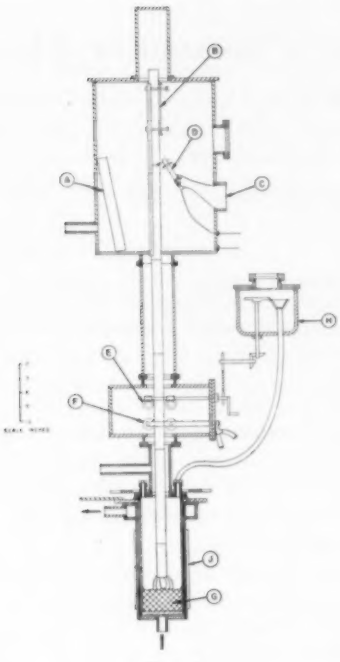

FIG. 1

composition which can be powdered for ease of distribution in the electrode pressing step. Most such brittle master alloys are very strong in compression and create a great problem in crushing. Use of the sharp, hard alloy particles also causes considerable increase in die wear during electrode pressing.

With metals which could be drawn or extruded to dimension, wires formed a very satisfactory form for addition. Dimension of the wire was controlled so that one, two, or three die lengths provided the exact amount desired. Shot was less desirable than wire as uniform distribution in the electrode was more of a problem.

All bar additions suffered certain drawbacks in operation, foremost of which was the formation of a low-melting eutectic in the hot electrode several inches above the point of melting, and consequent irregular "bleeding" of this alloy out of the bar. This resulted in a "banded" ingot of alternate layers of high and low alloy content. Further trouble occurred when the run was completed and the furnace opened for cleaning. The end of the electrode, for a distance of 6 in. back from the tip, was impregnated with heterogeneous alloys and intermetallic compounds which often were very pyrophoric or underwent rapid decomposition and oxidation, with the result that the routine operation often involved removal and rejection of this section of the electrode. In an attempt to avoid this, a series of tests on screw-feeders was made to determine the suitability of these devices for adding alloying powder to the

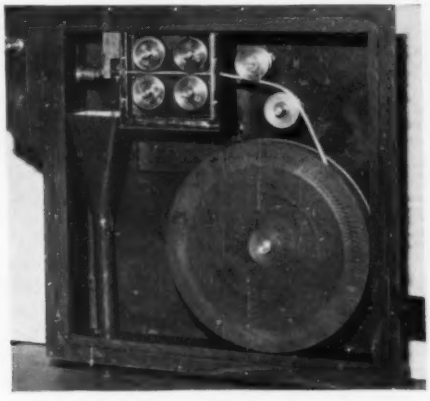

FIG. 2

molten pool. Due to an arc blast, "flotation" of powder with subsequent segregation, the nonavailability of some pure metal powders, and the high ingot specification, screw feeders were abandoned.

A particularly difficult problem arose in making additions of tin in the range of 1–5% to a series of ingots. This was solved by a mechanical wire feeding device as shown in Fig. 2. Extruded tin wire, ¼ in. in diameter, was loaded into the device on a large spool from which feed rolls delivered it to a revolving cutter. From the cutter the sections approximately ¼ in. long were fed directly to the molten metal pool in the melting furnace. By connecting the arc melting electrode drive to the tin cutting device through a timing arrangement, satisfactory proportioning was obtained.

A very effective means of alloy addition when satisfactory powders of the desired alloying agent can be obtained, is a pill feeding device. The powder, or blend of various powders, is fed to an automatic rotary tablet press which produces the compacts about 1 cm in diameter and ½ cm thick at a rate of 200/min with a deviation in weight of less than 0.05 g per 10 tablets weighing 20 g or 0.25% error. These are loaded in batch lots into a circular vibrating feeder which feeds individual tablets to a metering gear as shown in Fig. 3. The entire device is sealed in the melting furnace or an auxiliary box where it feeds the tablets to the molten pool at a rate proportional to electrode consumption. This alloy addition system has given the best results to date.

A further difficulty, while due in part perhaps to peculiarities of the zirconium-tin system, has been encountered in enough other metals to be a serious problem. Ingots made by means of the tin wire cutting device had an excellent appearance when machined, and, although external analyses were quite satisfactory, sections cut from the ingots showed inclusions of almost pure tin as indicated by the arrows in Fig. 4, caused by gravity segregation.

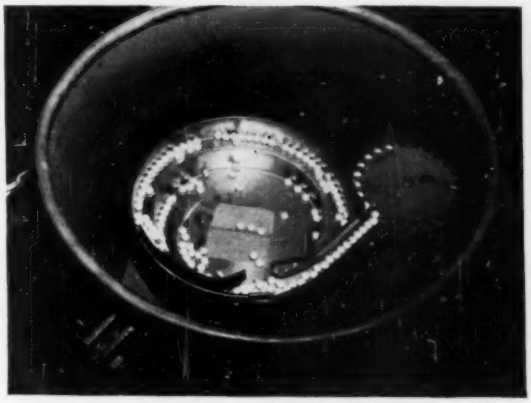

FIG. 3

These defective ingots were forged and rolled into 2 in. x 2 in. x 20 in. bars and fed through the furnace for remelting. Three tons of metal were produced by this method with considerable loss in forging and rolling due primarily to the inhomogeneities present in the core of the ingots. The yield of finished metal from sponge was in the order of 56%. In all cases the forging and rolling caused a hardening due to oxygen pickup as reported by Van Thyne and coworkers (5). Usual hardness increase in the tin alloy was 13 BHN.

In an effort to improve the unsatisfactory yield, the furnace was modified through the use of a d-c magnetic field created about the melting area by covering the entire water jacket from top to bottom with 3 layers of number 20 copper magnet wire (see Fig. 1). This device has been employed elsewhere for a somewhat different purpose (6). Here it was found that application of a small amount of direct current to the coil would cause the pool of molten metal inside the furnace to spin and mix. In this specific instance about 0.2 amp input was sufficient to give excellent stirring without centrifuging. Use of 1.4 amp on the coil caused heavy segregation of alloy particles in the outer surface of the ingot. Another effect of the stirring coil, perhaps as important in view of later developments as the stirring itself, is the arc control effect. Without a magnetic field applied the arc wanders at will and frequently localizes momentarily near one side of the crucible. The arc may later leave this spot so suddenly that it becomes deflected to the copper wall, with the result that the latter is instantly perforated and cooling water rushes in terminating the run. The magnetic field tends to center the arc, decreasing the possibility of ingot loss.

A slight improvement in yield was realized through the use of magnetic stirring of the metal pool, followed by rolling and remelting, and immediate needs

FIG 4

for alloy were met. However, increase in hardness, due to oxidation during these steps, plus losses mentioned in the forging and rolling, led to further efforts in the remelting work.

An obvious improvement was to produce an ingot in the first melting step which would serve as the electrode for remelting without forging and rolling. Such a system involving tungsten electrode melting has been described by Herres (7), but was not useful here since tungsten contamination was excessive.

The problem was solved by production of 6-in. diameter ingots in the first furnace and the remelting of these forms into an 8-in. final ingot. Addition of continuous ingot extraction as practiced by Gilbert and coworkers (8) has permitted production of single ingots long enough to provide the desired weight for remelting.

Design of the remelting furnace is identical with the first-melting furnace except for power application to the electrode. A typical furnace is shown in Fig. 5. The consumable electrode (A), made up in this case by nippling together several 6 in. diameter ingots, is supported by a water-cooled copper pipe (B). This assembly is lowered into the furnace by a geared winch (C). The entrance of the pipe into the furnace is sealed by a greased rubber "O" ring and packing gland (D). All other furnace parts are similarly sealed by rubber "O" rings permitting vacuum melting if this should be desirable. The furnace previously described cannot be operated under vacuum because of the various manipulations carried out by means of the rubber gloves which would stand, at best, only a few ounces of pressure differential.

In many cases vacuum melting is important since the zirconium sponge metal or the alloying agent may contain sufficient hydrogen to cause "rimming" or bubbling in the last portion of the ingot to freeze. Reduction of furnace pressure to 4 cm or less eliminates rimming, generally without causing other undesirable effects. Recent analyses indicate that ingots produced using a reduced pressure final melting

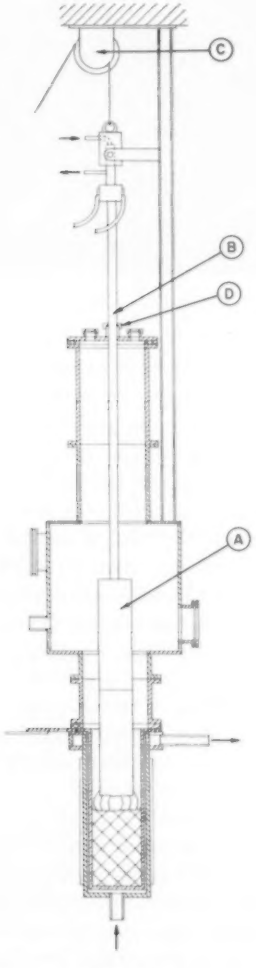

FIG. 5

step have a hydrogen content on the order of 15 ppm. A single stage mechanical vacuum pump having a free air rating of 110 ft³/min provides adequate vacuum for successful remelting and at the same time does not pump down under normal operation into the "glow discharge" range, which must be avoided for uniform results. This furnace can produce double melted ingots from 8 to 14 in. diameter.

Satisfactory ingots are produced using the following power inputs:

Ingot, diameter in.	2	3	4	5	6	7	8	9	10	14
Volts	25	28	30	38	40	40	40	40	40	40
Amperes	800	1000	1800	2500	3500	4000	4500	5000	5500	6000
Kilowatts	20	28	54	85	140	160	180	200	220	240

Energy input above this level is desirable only in an effort to reach maximum production rates per furnace operation hour. Use of as high as 160 kw (40 v—4000 Å) in the production of 5-in. diameter ingots has caused no difficulty.

Rate of melting and furnace efficiency vary slightly with different types of sponge metal and alloying agents, but under production conditions the rate of melting depends directly upon the power applied. Average power consumption for melting zirconium is about 0.25 kwhr/lb. This is based on the use of direct current, the electrode being cathodic. Employing the latest value for the heat content of zirconium at the melting point as furnished by Kelley (9) the above figure shows the furnace to have an electrical efficiency of about 50%. This is possible only because the heat is generated within the metal mass being melted.

Water consumption is variable, the quantity of water used being that required to carry off residual energy and to prevent steam pocket formation. Convenient practice is to circulate water from a cooling sump, thus permitting use of high flow rates which eliminate steam pocket formation. No effect upon furnace efficiency or ingot wall imperfections has been found possible by water control over the discharge temperature range of 37°–100°C. Usual rate employed for routine melting of a 10-in. ingot is 120 gal/min.

PURITY AND HOMOGENEITY

Ingots are machined on the surface to remove visible flaws and are then checked by means of a Sperry Ultrasonic Reflectoscope for shrinkage cavities or other internal flaws.

There are few steps that can be taken with an active metal like zirconium that do not add some contamination. While consumable electrode arc melting does not add carbon or tungsten, usually encountered in arc melting work, it does raise oxygen and nitrogen contamination. Oxygen is contributed by moisture often present in hygroscopic salts carried over in the sponge metal from the manufacturing process. Extensive exposure of sponge to moisture or use of sponge containing excessive residual chlorides must be avoided if low-oxygen metal is required. Further, experiments have shown that it is futile to attempt to dry zirconium sponge, once it has become damp, without expecting a significant increase in hardness. This is due partly to the hygro-

scopic nature of the entrapped magnesium chloride, and partly to the highly reactive surface of sponge zirconium which forms oxide and hydrogen from water at room temperature. Nitrogen contamination is due generally to atmospheric contamination during melting. Helium and argon employed in inert atmosphere melting do not contribute significant contamination since only one furnace filling of these gases is employed for each ingot.

Oxygen content of Kroll process zirconium ingot produced at the Bureau of Mines is now averaging around 1100 ppm. Procedures for determination of oxygen in zirconium metal are not highly accurate at present so contamination is reported in terms of nitrogen. Routine double melted 500-lb ingots gain 0.001% (10 ppm) nitrogen in processing from sponge to final form, indicating moderately good furnace technique. It may be inferred that very little oxygen is added by furnace operation since, under operating conditions, no selectivity for oxygen or nitrogen is considered likely.

The homogeneity of the ingots is illustrated by the case of tin, a most difficult metal to alloy properly with zirconium. Production analyses are made by a recording spectrograph which is arranged to make tests at 1-in. intervals down the side of the ingot, two passes being made at 90° to each other (10). The accuracy of the process was checked by sawing numerous ingots in half vertically and analyzing them internally also. Under certain circumstances tin was specified at 2.5%. Acceptability of the ingots was based on the range of tin values and the standard deviation, σ defined by

$$\sigma = \sqrt{\frac{\Sigma(\Delta)^2}{\eta}}$$

where Δ is the individual deviation from average and η is the number of analyses considered.

The first ingot in a series of ten to be discussed had the following analyses:

Position	Tin, %	Position	Tin, %
1	2.49	9	2.51
2	2.51	10	2.51
3	2.48	11	2.46
4	2.49	12	2.51
5	2.51	13	2.51
6	2.50	14	2.50
7	2.50	15	2.49
8	2.50		

This is admittedly a very good ingot having a standard deviation of only 0.01. The next nine ingots produced had standard deviations ranging from 0.02% to 0.08%.

Homogeneity of this degree compares favorably with other industrial techniques.

Effective Recovery and Economics

Production of pure zirconium ingots by a single melting operation gives 85% recovery of the sponge in the form of finished ingot, free of flaws. These ingots and all alloy ingots can be remelted economically since the effective recovery is increased to an average of 95% by this process due to an improved sidewall. This automatic increase in useful metal is important since the value of one pound of metal is equivalent to the electrical energy required to melt 4 tons of ingot. First benefit of consumable electrode double melting is thus that very little ingot scrap is produced.

Second advantage is found in the homogeneity of the small amount of turnings that are produced. It has been possible to clean these chips and combine them in later runs without any decrease in quality or change in analysis. A distinct effort must be made in the machine shop to cut a smooth, heavy chip that can be salvaged.

Finally, ingots without segregation and internal flaws seldom fail in forging and rolling and no "head crop" is necessary. The decrease in this type of scrap is quite important in the effective metal yield obtained by consumable electrode double melting.

Conclusions

It is felt that from the above information the following statements are in order in regard to the consumable electrode double melting technique.

1. There is no "electrode" contamination of carbon or tungsten.
2. The method produces homogeneity comparable to the best attainable commercially.
3. Scrap recovery is high in that only a small amount of scrap is produced and this is easily recovered.
4. Increase in effective metal recovery and decreased forging and rolling loss more than pays for remelting.
5. Simplicity of design, flexibility of the furnaces, and absence of specialized hard-to-get components makes possible the erection of such melting equipment at very low cost.

Acknowledgments

The work reported herein was carried out through the cooperation of The Naval Reactors Division of the Bureau of Ships on contract NPO 19905. The assistance of E. T. Hayes in the field of metallography and physical testing in conjunction with the work has been of great assistance. Recognition is made of the services of Floyd Wood, Physicist, and Lambert Woudenberg and Frank Wagy, plant foremen in this work.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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Concentration Polarization and Overvoltage[1]

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ABSTRACT

Concentration gradients exist at the electrodes in every electrolysis. This paper discusses the magnitude of concentration polarization to be expected in the measurement of hydrogen overvoltage, and demonstrates the use of the Nernst-Fick equation to calculate its effect, in acid, alkaline, and buffered solutions.

THEORETICAL ASPECTS

Theories of overvoltage deal with the chemical or electrochemical ("activation") polarization at an electrode surface. In any electrolysis, or other process at a solid-liquid interface, concentration gradients exist near the solid surface. Whether or not they are important in determining the rate of the process depends on the relative rates of reaction and of convective-diffusive transport at the surface. Theory and experiment have been thoroughly reviewed, with respect to both dissolution rates (1) and electrode processes (2). It is especially important to avoid, or recognize and correct for, concentration polarization in overvoltage measurements.

The rate of diffusive transport to or from an electrode surface may be expressed by the Nernst equation

$$\dot{n} = D\Delta c/\delta \qquad \text{(I)}$$

where $\dot{n}$ designates equivalents transported per second per cm², D is the diffusion coefficient in cm²/sec, Δc is the difference in surface and bulk concentrations in equiv/cm³, and δ is the "effective thickness" of the boundary layer (thickness it would have if the gradient were linear with distance). D varies with reagent concentration and other factors, δ is highly dependent on stirring speed and to the $\frac{1}{5}$ to $\frac{1}{3}$ power of D (1).

This equation may be applied very simply to calculate surface concentrations in polarization experiments, provided the solution composition is suitable and precautions are taken to insure constancy of D and δ. It may be written as follows:

$$\Delta C = 10^3 \frac{\delta}{D} \frac{i}{\mathbf{F}} \qquad \text{(II)}$$

where i = current density in amp/cm², $\mathbf{F}$ is the faraday, and C is now concentration in equiv/liter. For calculations it is necessary to know δ and D under the particular conditions employed, and these may be measured by supplementary experiments.

Many hydrogen and oxygen overvoltage measurements have been made with stirring by gas bubbles and at a total electrolyte concentration of 0.1N–1.0N. The approximate value of δ has been determined under these conditions, at room temperature, as follows.[2] The rate of dissolution of strips of zinc of 13 cm² area was measured, in 50 cm³ of solution containing (*a*) 0.0200M HCl, 0.06M KNO_3, 0.50M NaCl; (*b*) 0.0229N H_2SO_4, 0.06M KNO_3, 0.50N Na_2SO_4. The solutions were stirred with nitrogen, the dissolution rate increasing with the speed of bubbling. At the highest practical bubbling rate, solution (*a*) dissolved an average of 16.9 mg in 4 min, solution (*b*) an average of 13.3 mg in 4 min. This is a first order, diffusion-controlled process, and δ is calculated from the integrated Nernst equation:

$$\frac{D}{\delta} = \frac{2.3V}{At} \log \frac{a}{a - x} \qquad \text{(III)}$$

where A = area, V = solution volume in cm³, a = total dissolving capacity (29.7 and 34.0 mg, respectively, by experiment), and x = amount dissolved at time t.

Values of D used in these and other calculations below are listed in Table I (3, 4). The above experiments give δ = 0.0048 and 0.0044 cm; 0.005 cm has been used in the calculations below, with $\mathbf{F} = 10^5$ coulombs. Neither D nor δ varies much with reasonable changes in concentration of acid, base, salt, or buffer, and no attempt has been made to secure exact values for any particular case. Gas evolution at the electrode surface probably has little effect on δ in the current range considered here.

Gas bubbling is a rather ineffective means of stirring. With a metal cylinder rotating at a peripheral speed of 160,000 cm/min, with baffles to prevent cavitation and splashing, δ is reduced to about 1.5×10^{-4} cm (5). With a thin wire mounted near a grooved 2 cm shaft rotating at 4000 rpm, δ is 6 or 7×10^{-4} cm (6). It has been claimed (7) that

[1] Manuscript received September 9, 1954.

[2] Experiments by Eric Rau.

TABLE I. *Some values of D, the diffusion coefficient, at 25°C*

0.05*N* HCl	3×10^{-5} cm²/sec
0.05*N* HCl + 0.5*N* NaCl	6.5×10^{-5}
Dil. NaOH	2×10^{-5}
Dil. NaOH + 0.5*N* NaCl	4×10^{-5}
Dil. H_2SO_4	2×10^{-5}
Dil. H_2SO_4 + 0.1*N* $MgSO_4$	3.3×10^{-5}
Dil. H_2SO_4 + 0.5*N* $MgSO_4$	3.5×10^{-5}
0.05*N* acetic acid + 0.1*N* $Mg(C_2H_3O_2)_2$	1.25×10^{-5}

TABLE II. *Surface C_{H^+} as function of current density for 0.1N H_2SO_4, assuming $D = 3.3 \times 10^{-5}$ cm²/sec, $\delta = 5 \times 10^{-3}$ cm*

i, amp/cm²	ΔC_{H^+}, mpl	ΔpH	ΔE_{rev}, volt
10^{-3}	1.5×10^{-3}	0.01	0.001
10^{-2}	1.5×10^{-2}	0.07	0.004
2.5×10^{-2}	3.75×10^{-2}	0.20	0.011
5×10^{-2}	7.5×10^{-2}	0.40	0.035
7.5×10^{-2}	>0.1	>6	>0.41

the boundary layer is reduced to negligible thickness at a small rotating platinum wire mounted near a glass bladed stirrer also rotating at 600–1100 rpm. This claim seems improbable; limiting currents given by the authors suggest a thickness of about 10^{-3} cm.

Neutral salt solutions.—Imagine a salt solution like 0.5*N* NaCl, in pure water and quite neutral, so that $C_{H^+} = C_{OH^-} \cong 1.4 \times 10^{-7}$ moles/l [for the ionization of water in salt solutions see reference (8)]. An inert cathode is introduced and the solution is stirred by gas bubbling. Most of the current is carried by other ions, and OH^- ions produced leave the cathode surface by diffusion (i.e., the transference number $t_{OH^-} \to 0$). Numerical values may be inserted in equation (II):

$$\Delta C_{OH^-} = 10^3 \frac{5_{\delta} \times 1_{\delta} 10^{-3}}{4 \times 10^{-5}} \frac{i}{10^5} = 1.25i$$

This equation is not valid at $i < 10^{-6}$ amp/cm² because of the slight buffering action of water, but when $i > 10^{-5}$ amp/cm² this effect will be negligible. It is assumed that the volume of solution is large or that current is passed too briefly to affect the bulk pH.

Each tenfold increase in current density, above $i = 10^{-6}$, will increase the surface pH by one unit, and the reversible emf of a hydrogen electrode (E_{rev}) will change by 0.059 v (the activity coefficients of H^+ and OH^- are independent of concentration in this "swamping" salt solution, and junction potential between the surface and the bulk of solution is negligible). A "Tafel plot" with slope of 0.059 would be obtained with no "activation polarization" whatsoever.

If a weak base should be present in the salt solution, it will have very little buffer capacity toward OH^- ions and similar concentration polarization will result. The slope will approach 0.059 at a slightly higher pH.

Acid solutions.—It is obvious that for each acid solution a sharp rise in surface pH occurs when ΔC_{acid} approaches the original C_{acid}—as the "limiting current" is approached. This is illustrated in Table II and with several curves in Fig. 1, where ΔE_{rev} is plotted vs. log i.

If the current is increased beyond the acid diffusion current, the cathode surface becomes alkaline, and the curve continues as shown in Fig. 2 for 0.001M HCl in 0.5M NaCl. In this particular case equation (II) can be applied up to $i = 1.3 \times 10^{-3}$,

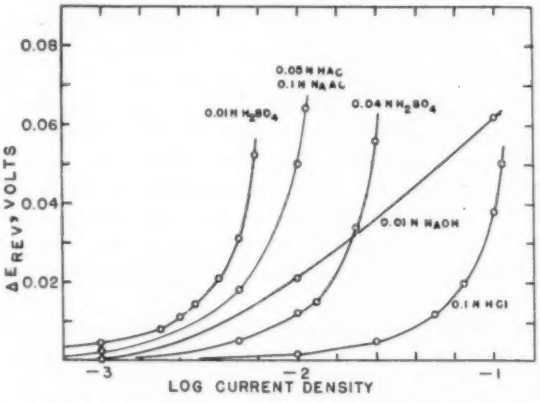

FIG. 1. Concentration polarization in various solutions. Sulfuric acid solutions to contain 0.5*N* sulfate; HCl and NaOH solutions to contain 0.5*N* NaCl. Circles are calculated points.

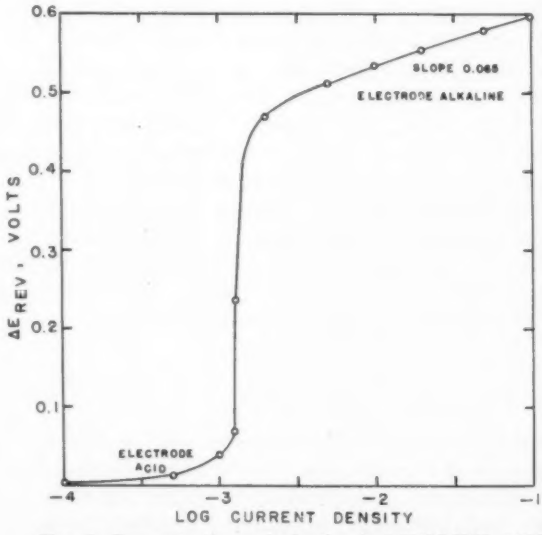

FIG. 2. Concentration polarization in 0.001M HCl, 0.5M NaCl. Circles are calculated values.

when the surface pH rises to 7. At higher current density OH^- ion is produced in excess and, as it diffuses outward, it is met and neutralized by the acid, at a plane within the boundary layer which we may say is $y\delta$ distant from the surface. Equation (I) may be modified as follows (3), since acid and base diffuse in equivalent amounts:

$$\dot{n} = \frac{D_{OH^-} c_{OH^-}}{y\delta} = \frac{D_{H^+} c_{H^+}}{(1 - y)\delta} \qquad (IV)$$

When $10^3\ c_{OH^-}$ and $10^3\ c_{H^+}$ are $\gg 1.4 \times 10^{-7}$M they are equivalent to the previous ΔC's.

For calculation of the surface C_{OH^-} and E_{rev}, y may be eliminated and $i/\mathbf{F}$ substituted for $\dot{n}$:

$$C_{OH^-} = \frac{i/\mathbf{F} - 10^{-3} D_{H^+} C_{H^+}}{10^{-3} D_{OH^-}} \qquad (V)$$

where the C's are in moles/liter. With a high concentration of supporting electrolyte, changes in activity coefficients, and junction potential, may again be neglected.

Since in the alkaline surface range a reversible hydrogen electrode, if placed immediately at the cathode surface, would show a potential of 0.5 v or more with respect to one in the bulk of the solution, apparent overvoltage should be corrected accordingly.[3] Curves similar to that of Fig. 2 would be obtained with weak acid or acid buffers. All the curves for acids in Fig. 1 would be similar at higher current densities. The curve in the alkaline region in Fig. 2 is nearly, though not quite, linear with an average slope of 0.065. The more acid in the solution, the higher this slope will be.

Buffer solutions.—With a buffer consisting of a weak acid and its salt, appreciable concentration polarization is found at a lower current density than with the same concentration of strong acid, as shown for an acetate buffer in Fig. 1. This is because pH depends on the ratio acid/salt, and as surface C_{acid} decreases, surface C_{salt} increases by an equal amount. Equation (II) may be employed for calculation except at extreme acid/salt ratios. Alkaline buffers consisting of an acid molecule and its reciprocal base may be treated in the same way, provided the cathode reaction remains simple neutralization of the acid component. If hydroxyl ion is produced in excess at the surface this becomes an interdiffusion problem as described above.

Strong base solution.—Fig. 1 shows the concentration polarization curve to be expected if the starting solution is 0.01N NaOH in 0.5N NaCl. The slope is smaller than 0.059 v/unit log i, approaching this value at sufficiently high current density.

[3] Note, however, that the remaining curve would refer to a surface solution whose composition varies with current density.

Acid alone.—If no indifferent salt (supporting electrolyte) is present, the fraction t_{H^+} of the cathode current is carried by ion migration, and only $(1 - t_{H^+})$ by diffusion. Equation (II) should be modified:

$$\Delta C_{H^+} = (1 - t_{H^+})\ 10^3 \frac{\delta}{D} \frac{i}{\mathbf{F}} \qquad (VI)$$

where t_{H^+} is the transference number. Concentration polarization becomes appreciable at a somewhat higher current density. In 0.1N H_2SO_4, 0.5N $MgSO_4$, with $\delta = 5 \times 10^{-3}$ cm

$$\Delta C = 1.43\ i$$

In 0.1N H_2SO_4 alone, with $t_{H^+} = 0.82$ (8)

$$\Delta C = 0.45\ i$$

Over a wide range of ΔC, the change in t_{H^+} with concentration should be considered.

In solutions of acid alone, concentration polarization measurements may also be extended beyond the acid diffusion (and migration) current; Coates (9), using an interrupter method to separate the concentration effect from true overvoltage, has shown that the curves look much like Fig. 2, with even larger increases in potential. If actually no positive ions except H^+ are present, an equilibrium pH above 7 seems impossible. Coates postulates an excess of OH^- ions, and lack of electroneutrality at the cathode surface, forced by the current flow; a very small excess C_{OH^-} in the abnormal electrical double layer would account for an apparent pH of 20 or more. This is neither normal concentration polarization nor activation polarization in the usual sense.

Discussion

Breaks in hydrogen overvoltage curves from Tafel slopes of about 0.03 to slopes of about 0.1 have been found in acid and buffer solutions by Schuldiner (10). These breaks appear at current densities where equation (II) predicts the existence of appreciable concentration polarization. Current densities plotted by Schuldiner are based on electrode roughness factors of about 2, and in comparing with the present treatment i must be based on apparent area, since δ is not much affected by very small surface irregularities. The breaks to higher slopes follow regularly with increasing acid concentration, and are predicted rather closely with δ a little smaller than 0.005 cm. Adequate correction of the curves requires a more precise value of D and a knowledge of whether δ is affected by gas evolution in addition to the stirring by hydrogen bubbling. In the meantime, changes in slope can be given

little significance. In only one case did Schuldiner continue measurements to high enough currents to obtain a curve like Fig. 2.

Uniform overvoltage curves were found by Bockris and Azzam (11), in 5*N* HCl, to current densities of the order of 100 amp/cm². These authors were well aware of the danger of including concentration polarization in the measurements, and attempted to calculate the current at which it would be appreciable. While their method of calculation was not well suited to the experimental conditions, and the value (0.01 cm) chosen for δ was certainly incorrect, they were probably correct in assigning another reason for the breaks in slope found at the highest current densities. Equation (VI) could be applied directly; D and t_{H^+} can be sufficiently well estimated, but δ would have to be found, since the intense hydrogen evolution at very high current densities would certainly decrease its value below 0.005 cm.

Cathodic polarization measurements on titanium and zirconium electrodes in sodium chloride solutions have been made by Hackerman and his students (12, 13). While these were not intended as precise overvoltage measurements, they illustrate the uncertainty of interpretation. The solutions perhaps had a small buffer capacity, and at small currents the cathode potential remained low because of oxygen reduction, even though the surface solution became alkaline. The sharp rises observed were due, as the authors state, to limiting oxygen diffusion currents. In the hydrogen evolution region the authors give the equations for E vs. the saturated calomel cell

$$E = -1.93 - 0.154 \log i \text{ titanium}$$

$$E = -1.47 - 0.15 \log i \text{ zirconium}$$

Provided δ does not vary with current, both slopes should be corrected by about 0.06. Correction of the constants is less certain; if surface pH = 7 when $\log i = -6$, then 1.01 v is found, including the calomel cell potential. The overvoltage equations become—for alkaline solutions of varying composition—:

$$\eta = 0.92 + 0.094 \log i \text{ titanium}$$

$$\eta = 0.46 + 0.09 \log i \text{ zirconium}$$

For the case of a single diffusing species whose concentration can fall to zero at the electrode surface, the method described above is equivalent to use of the well-known relation

$$E_{rev} = \frac{RT}{n\mathbf{F}} \ln \frac{i_d - i}{i_d} \qquad \text{(VII)}$$

where i_d is the diffusion or limiting current density. This equation is derived on the same premises as equation (II), but assumes D and δ to be constant, while different values can be inserted in equation (II) for each current density, if required. Coates (9) shows that, with no stirring except cathodic hydrogen evolution, experimental concentration polarization is greater than equation (VII) predicts, simply because δ decreases with increasing current density. This is equivalent, in equation (VII), to an increase in i_d for each increase in i.

With auxiliary stirring, does gas evolution at the electrode cause δ to decrease with current density? At relatively high stirring speeds, hydrogen evolution when magnesium dissolves in acids does not appear to affect δ much (4). In the present case, the same is probably true until stirring by gas evolution alone approaches the auxiliary stirring alone. Comparison with magnesium dissolution indicates that this would occur (i. e., $\delta = 0.005$ cm) at a current density somewhat above 0.1 amp/cm² (14). At lower currents δ is probably constant, but this should be tested by experiment.

Not all investigators can agree with Coates that forced electrolysis in a solution of pure acid leads to lack of electroneutrality at the cathode surface, or that his measured potentials in this region have been interpreted correctly. However, could not a smaller degree of charge separation be present in every electrolysis, and vitiate any calculation of concentration polarization? There is no experimental evidence to suggest such an effect for ordinary solutions. With sufficient supporting electrolyte, or with current densities low compared to total concentration, the Nernst emf equation can be employed with confidence.

What recommendations can be made concerning the composition of solutions to be used in hydrogen overpotential measurements? It seems better to avoid corrections for concentration polarization so far as possible, since these entail some uncertainty at best. Further, it is desirable to measure overvoltage as a function of both current density and composition of solution, and it is obviously preferable to change these variables separately. No difficulties are encountered in concentrated strong acid or base solutions, except at very high current densities. With neutral salts, correction is almost unavoidable. Reliable measurements are highly desirable in dilute acid and base solutions and in buffers around the neutral point. There is no doubt a change in Tafel slope in acid and alkaline solutions, and it would be useful to know just how and where this occurs. In this region concentration polarization is sure to be present except at the lowest current densities and, if it is undesirable to

make direct corrections for it, at least its magnitude can be calculated and its effect studied.

In this paper no assumptions have been made concerning the mechanism of hydrogen discharge, or the nature and magnitude of "activation" overpotential; indeed, such assumptions were quite unnecessary for the purpose. Concentration polarization is directly related to current density and the other factors considered, but of course has nothing to do with the discharge mechanism.

Similar treatment can naturally be applied to anodic oxygen evolution, to metal deposition, to oxidation-reduction processes at inert electrodes, etc. More thorough and elegant treatment of some of these cases has been made by Petrocelli (15) and by Eisenberg, Tobias, and Wilke (16).

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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A Theoretical Basis for a New Method of Investigating Corrosion Inhibition[1]

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ABSTRACT

An inequality has been derived that bounds the derivative of the corrosion current with respect to the concentration of a strictly cathodic inhibitor:

$$\left|\frac{\partial I_1}{\partial x}\right| \leq \frac{\left|\frac{\partial \Gamma}{\partial x}\right|}{\left|\frac{\partial \Gamma}{\partial I_2} + W\right|}.$$

(See text for definition of terms.)

In special cases the inequality is a direct consequence of Cupr's generalization of Müller's electrochemical model of corrosion. In the general case it is necessary to invoke a statistical assumption to obtain the same result. The upper bound of the derivative can be calculated from measurements of the potential difference between a corroding electrode and a reference half-cell at different concentrations of the inhibitor and at different densities of an externally applied current. If the upper bound is small, the agent under investigation is definitely not a good cathodic inhibitor, although it may or may not be a good anodic one. If the upper bound is large, no conclusion can be drawn; some other method must be employed to determine whether the agent is an effective inhibitor. Therefore, what the theory provides is a rapid method for screening cathodic inhibitors to eliminate from further consideration certain ones that can be shown ineffective. If the Müller-Cupr model is a valid one, there is no obvious way of accomplishing more than this by means of potential measurements alone.

INTRODUCTION

Mears (1) has shown that the direction of potential shift of a corroding metal surface following adsorption of a chemical additive is not a dependable indication of whether the additive is functioning as an inhibitor. Furthermore, the magnitude of the shift is not necessarily a measure of the effectiveness of the additive in those cases in which a known inhibitor alters the potential to a more noble value. Unfortunately these observations imply that the once much-used technique of screening inhibitors by means of potential measurements is not a trustworthy one. Mears' conclusions, based implicitly on Müller's (2) electrochemical model of corrosion and on its generalization by Cupr (3), apply to potential measurements of metals in inhibited solutions when no external current is imposed across the metal-solution interface. This paper shows that there is a theoretical basis for screening cathodic inhibitors by means of a function that may be determined by potential measurements when an external current is applied.

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The conclusions to be drawn here, like those of Mears, are based on Cupr's concept of a corroding metal surface. Before examining this matter in detail it is worth while to list some of the conventions that have been adopted in this paper. In the preceding paragraph the word *potential* was used in its electrochemical sense. From here on it refers to the work required to bring a unit electrical charge to a point. A potential E_o will be assigned arbitrarily to some point, α, in the system under consideration. Then, at any other point, β, to which a potential is assigned the potential is E_o plus a potential difference between α and β defined in the usual way. Current flows from a point of higher (more positive) to a point of lower (less positive) potential in any region not containing points of discontinuity of potential, regardless of whether the current is electronic or ionic. As an exception to this rule, small ohmic potential drops in metals are neglected, i.e., a metal may be assumed to be at constant potential even though it carries a small current. Points of discontinuity of potential in a circuit are denoted by the usual symbol (a) illustrated in Fig. 1. Current may flow in either direction across such a point. However, if the point of discontinuity is the only source of

electromotive force in a closed circuit, the direction of current flow is that shown by the arrow in Fig. 1 regardless of whether the current is ionic or electronic. At the risk of some confusion the expression *half-cell potential* will be given an electrochemical meaning different from the meaning of *potential* just discussed. Specifically, if there is no current flowing across the interface between a solution and a reference half-cell or in the lead wire to the half cell, and if $V(\alpha)$ is the potential at an arbitrary point, α, of the (equipotential) lead wire and $V(\beta)$ is the potential at an arbitrary point, β, of the (equipotential) interface, then $\Theta = V(\beta) - V(\alpha)$ will be defined to be the half-cell potential.

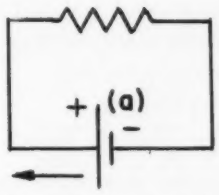

FIG. 1. Potential discontinuity; direction of current flow

THEORY

According to Cupr a metal electrode corroding in an electrolyte may be represented symbolically by the network of Fig. 2 in which N local cells are arranged in parallel between two equipotential surfaces. One of these is the metal-solution interface and the other is the electrode boundary, the significance of which is discussed by Cupr and by Pearson (4). The interface to be discussed here is roughly plane and the electrode boundary is approximately a plane located in the electrolyte "parallel" to the interface at a distance from it that may be determined experimentally. The electrolyte outside the electrode boundary is assumed to be homogeneous; hence, if an external current is made to flow from a remote source through the electrolyte to the boundary, the lines of flow outside the boundary will be perpendicular to it and the equipotentials will be planes parallel to it. The current density outside the boundary is, of course, constant.

Consider a j^{th} arbitrary local cell in Fig. 2. The local anode components are R_{1j}, a resistance, and E_{1j}, a point discontinuity in potential that constitutes the "driving force" for the corrosion current in this j^{th} local cell. Similarly, the cathode components are R_{2j} and E_{2j}. E_{2j} represents the solution pressure and back emf of polarization at the j^{th} cathode. The phenomenon of anode polarization is taken into account by making E_{1j} and R_{1j} variables. I_{1j} is the current in the anode branch of the j^{th} cell, and I_{2j} is the current in the cathode branch. If no external current is applied to the j^{th} cell, I_{1j} and I_{2j} are equal, are not zero, and flow in the directions indicated by the arrows in the figure. The component of the external current that enters the j^{th} cell is I_{3j}. For sufficiently large values of I_{3j} (note direction in Fig. 2), the direction of I_{1j} may be reversed. If, when this happens, I_{1j} is defined to be a negative quantity, and if I_{2j} and I_{3j} are always taken to be positive or zero, all of the equations that follow remain valid

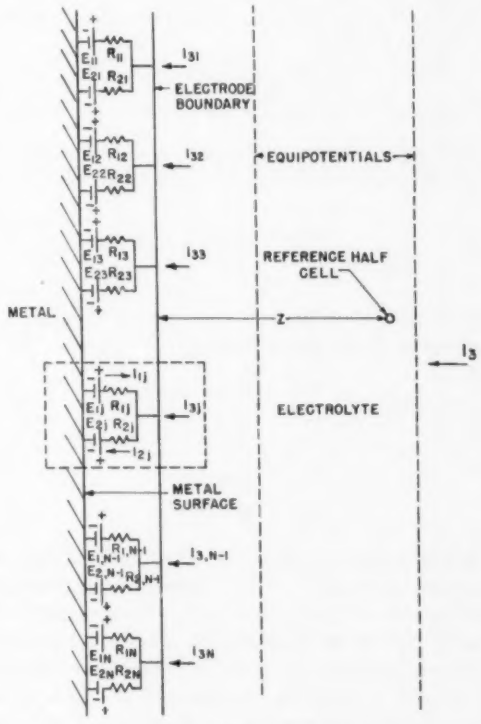

FIG. 2. The Müller-Cupr model

regardless of the direction of the currents at the local anodes.[2]

In order not to complicate the problem unnecessarily the resistivity, ρ, of the electrolyte is considered to be constant, although in fact it might depend to a small extent on the concentration, x, of an inhibitor. This is not a crucial point; corrections for variations in ρ can be made if necessary. Because of the convention stated above concerning current directions N, the number of local cells, is a constant. The total anode current in the N cells is

$$I_1 = \sum_{j=1}^{N} I_{1j} \qquad [1]$$

[2] In general, it should be noted that the second subscript following a symbol identifies the local cell to which the symbol pertains. The range of this subscript is 1 to N. The first subscript will always be a 1, 2, or 3; 1 indicates an anode component, 2 a cathode component, and 3 (used always with I) an externally applied current.

Faraday's law implies that I_1 is directly proportional to the rate of corrosion of the metal under test. The total external current applied is

$$I_3 = \sum_{j=1}^{N} I_{3j} \qquad [2]$$

If A is the area of the metal surface and z is the distance between the electrode boundary and a reference half-cell located outside the electrode boundary (see Fig. 2), the resistance between the boundary and the half-cell is:

$$W = \frac{\rho z}{A} \qquad [3]$$

It is assumed that the resistive and emf components of each local cell are functions of the inhibitor concentration and the current through the component. That is, for each j:

$$\begin{aligned} E_{1j} &= E_{1j}(x, I_{1j}) \\ E_{2j} &= E_{2j}(x, I_{2j}) \\ R_{1j} &= R_{1j}(x, I_{1j}) \\ R_{2j} &= R_{2j}(x, I_{2j}) \end{aligned} \qquad [4]$$

This is a natural, but by no means inevitable, assumption. It would not hold over a long period of time because of the accumulation of corrosion products on the metal surface and because of gradual changes in location of the active centers of corrosion. Nor would it hold, for example, in the case of an inhibitor for which the extent of adsorption depends on whether the inhibitor is added before or after an external current is applied.

The half-cell potential of the reference half-cell is called Θ. If α is an arbitrary point in the lead wire to the half-cell, a potentiometer connected to the lead wire and to the corroding metal measures a potential difference, Γ:

$$\Gamma = E_o - V(\alpha)$$

where E_o is the potential arbitrarily assigned to the metal and $V(\alpha)$ is the potential at α. If β is a point on the interface between the half-cell and the solution:

$$\Theta = V(\beta) - V(\alpha)$$

Also from Ohm's and Kirchoff's laws for each j:

$$V(\beta) = E_o + E_{1j} - I_{1j}R_{1j} + I_3W$$

Combining these last three equations:

$$\Gamma = \Theta - E_{1j} + I_{1j}R_{1j} - I_3W \qquad [5]$$

Of course when Θ and I_3 are zero, and I_{1j} vanishes for every j, $-\Gamma$ becomes the thermodynamic half-cell potential of the metal. Application of the principle of superposition of currents and Kirchoff's laws to the j^{th} cell yields the well-known equations [see reference (4) for example]:

$$\begin{aligned} I_{1j} &= \frac{E_{1j} - E_{2j}}{R_{1j} + R_{2j}} - \frac{R_{2j}I_{3j}}{R_{1j} + R_{2j}} \\ &= \phi_1(E_{1j}, E_{2j}, R_{1j}, R_{2j}, I_{3j}) \end{aligned} \qquad [6]$$

$$\begin{aligned} I_{2j} &= \frac{E_{1j} - E_{2j}}{R_{1j} + R_{2j}} + \frac{R_{1j}I_{3j}}{R_{1j} + R_{2j}} \\ &= \phi_2(E_{1j}, E_{2j}, R_{1j}, R_{2j}, I_{3j}) \end{aligned} \qquad [7]$$

Differentiation of [6] yields

$$dI_{1j} = \frac{\left[dE_{1j} - dE_{2j} + \frac{(-E_{1j} + E_{2j} + R_{2j}I_{3j})dR_{1j}}{R_{1j} + R_{2j}} + \frac{(-E_{1j} + E_{2j} - R_{1j}I_{3j})dR_{2j}}{R_{1j} + R_{2j}} - R_{2j}dI_{3j}\right]}{(R_{1j} + R_{2j})}$$

Or in view of [6] and [7],

$$dI_{1j} = \frac{(dE_{1j} - dE_{2j} - I_{1j}dR_{1j} - I_{2j}dR_{2j} - R_{2j}dI_{3j})}{(R_{1j} + R_{2j})} \qquad [8]$$

On differentiating the equations [4],

$$\begin{aligned} dE_{1j} &= \frac{\partial E_{1j}}{\partial x}dx + \frac{\partial E_{1j}}{\partial I_{1j}}dI_{1j} \\ dE_{2j} &= \frac{\partial E_{2j}}{\partial x}dx + \frac{\partial E_{2j}}{\partial I_{2j}}dI_{2j} \\ dR_{1j} &= \frac{\partial R_{1j}}{\partial x}dx + \frac{\partial R_{1j}}{\partial I_{1j}}dI_{1j} \\ dR_{2j} &= \frac{\partial R_{2j}}{\partial x}dx + \frac{\partial R_{2j}}{\partial I_{2j}}dI_{2j} \end{aligned} \qquad [9]$$

Substitution of the values of dE_{1j}, dE_{2j}, dR_{1j}, and dR_{2j} given by [9] in equation [8] yields after rearrangement:

$$\begin{aligned} dI_{1j}\left(R_{1j} + R_{2j} - \frac{\partial E_{1j}}{\partial I_{1j}} + I_{1j}\frac{\partial R_{1j}}{\partial I_{1j}}\right) \\ = \left(\frac{\partial E_{1j}}{\partial x} - \frac{\partial E_{2j}}{\partial x} - I_{1j}\frac{\partial R_{1j}}{\partial x} - I_{2j}\frac{\partial R_{2j}}{\partial x}\right) \\ dx - \left(\frac{\partial E_{2j}}{\partial I_{2j}} + I_{2j}\frac{\partial R_{2j}}{\partial I_{2j}}\right)dI_{2j} - R_{2j}dI_{3j} \end{aligned} \qquad [10]$$

Kirchoff's laws imply that for every j,

$$I_{2j} = I_{1j} + I_{3j} \qquad [11]$$

Therefore

$$dI_{2j} = dI_{1j} + dI_{2j}$$

On substituting this value of dI_{2j} in [10]

$$dI_{1j} \cdot \left(R_{1j} + R_{2j} - \frac{\partial E_{1j}}{\partial I_{1j}} + I_{1j}\frac{\partial R_{1j}}{\partial I_{1j}} + \frac{\partial E_{2j}}{\partial I_{2j}} + I_{2j}\frac{\partial R_{2j}}{\partial I_{2j}}\right) = \left(\frac{\partial E_{1j}}{\partial x} - \frac{\partial E_{2j}}{\partial x} - I_{1j}\frac{\partial R_{1j}}{\partial x} - I_{2j}\frac{\partial R_{2j}}{\partial x}\right) \cdot dx - \left(\frac{\partial E_{2j}}{\partial I_{2j}} + I_{2j}\frac{\partial R_{2j}}{\partial I_{2j}} + R_{2j}\right) dI_{3j} \quad [12]$$

For reasons that will become apparent later it is useful to define

$$\lambda_j = R_{1j} - \frac{\partial E_{1j}}{\partial I_{1j}} + I_{1j}\frac{\partial R_{1j}}{\partial I_{1j}}$$

$$\mu_j = R_{2j} + \frac{\partial E_{2j}}{\partial I_{2j}} + I_{2j}\frac{\partial R_{2j}}{\partial I_{2j}} \quad [13]$$

$$\Delta_j = \frac{\mu_j}{\lambda_j + \mu_j} \text{ (provided } \lambda_j + \mu_j \gtrless 0)$$

$$\psi_j = \frac{\partial E_{1j}}{\partial x} - I_{1j}\frac{\partial R_{1j}}{\partial x}$$

The coefficient of dI_{1j} in equation [12] is $(\lambda_j + \mu_j)$, and the coefficient of dI_{3j} is μ_j. Therefore,

$$\frac{\partial I_{1j}}{\partial I_{3j}} = -\Delta_j \quad [14]$$

$$\frac{\partial I_{1j}}{\partial x} = \frac{\left(\psi_j - \frac{\partial E_{2j}}{\partial x} - I_{2j}\frac{\partial R_{2j}}{\partial x}\right)}{\lambda_j + \mu_j} \quad [15]$$

After elimination of E_{1j}, E_{2j}, R_{1j}, R_{2j}, and I_{2j} among equation [6], the four equations [4], and equation [11], I_{1j} may be expressed as a function of x and I_{3j} only as is implicit in [12], [14], and [15]. Then:

$$dI_{1j} = \frac{\partial I_{1j}}{\partial x}\,dx + \frac{\partial I_{1j}}{\partial I_{3j}}\,dI_{3j} \quad [16]$$

Substituting [14] in [16]:

$$dI_{1j} = \frac{\partial I_{1j}}{\partial x}\,dx - \Delta_j dI_{3j} \quad [17]$$

From Kirchoff's laws and the principle of superposition of currents it is easily deduced that

$$I_{3j} = H_j I_3 \quad [18]$$

where

$$H_j = \frac{\left(\frac{1}{R_{1j}} + \frac{1}{R_{2j}}\right)}{\sum_{k=1}^{N}\left(\frac{1}{R_{1k}} + \frac{1}{R_{2k}}\right)} \quad [19]$$

Summation of [19] on j from 1 to N yields

$$\sum_{j=1}^{N} H_j = \frac{\sum_{j=1}^{N}\left(\frac{1}{R_{1j}} + \frac{1}{R_{2j}}\right)}{\sum_{k=1}^{N}\left(\frac{1}{R_{1k}} + \frac{1}{R_{2k}}\right)} = 1; \quad [20]$$

and differentiating [20]

$$\sum_{j=1}^{N} dH_j = 0 \quad [21]$$

Since Θ and W are constants it follows from [5] that for each j,

$$d\Gamma = -dE_{1j} + I_{1j}dR_{1j} + R_{1j}dI_{1j} - WdI_3$$

Combining this last equation with [9], [13], and [17]:

$$d\Gamma = \left(\lambda_j\frac{\partial I_{1j}}{\partial x} - \psi_j\right)dx - \lambda_j\Delta_j dI_{3j} - WdI_3 \quad [22]$$

From [18],

$$dI_{3j} = H_j dI_3 + I_3 dH_j \quad [23]$$

Combining [22] and [23],

$$d\Gamma = \left(\lambda_j\frac{\partial I_{1j}}{\partial x} - \psi_j\right)dx - (\Delta_j\lambda_j H_j + W) \cdot dI_3 - \Delta_j\lambda_j I_3 dH_j \quad [24]$$

Since I_3 and x may be varied independently,

$$\frac{\partial x}{\partial I_3} \equiv \frac{\partial I_3}{\partial x} \equiv 0$$

However H_j is a complicated function of both I_3 and x so that in general,

$$\frac{\partial H_j}{\partial x} \gtrless 0$$

$$\frac{\partial H_j}{\partial I_3} \gtrless 0$$

Therefore,

$$\frac{\partial \Gamma}{\partial x} = \left(\lambda_j\frac{\partial I_{1j}}{\partial x} - \psi_j\right) - \lambda_j\Delta_j I_3\frac{\partial H_j}{\partial x} \quad [25]$$

$$\frac{\partial \Gamma}{\partial I_3} = -\lambda_j\Delta_j\left(H_j + I_3\frac{\partial H_j}{\partial I_3}\right) - W \quad [26]$$

By solving [26] for λ_j, substituting the expression so obtained in [25] and solving for $\partial I_{1j}/\partial x$ one finds:

$$\frac{\partial I_{1j}}{\partial x} = \frac{\Delta_j\left[\left(\frac{\partial \Gamma}{\partial I_3} + W\right)I_3\frac{\partial H_j}{\partial x} - \left(\frac{\partial \Gamma}{\partial x} + \psi_j\right)\left(H_j + I_3\frac{\partial H_j}{\partial I_3}\right)\right]}{\left(\frac{\partial \Gamma}{\partial I_3} + W\right)} \quad [27]$$

Advantage may be taken of the monotonic nature of anode and cathode "polarization curves" to prove that for every j,

$$\lambda_j \geq 0$$

$$\mu_j \geq 0 \quad [28]$$

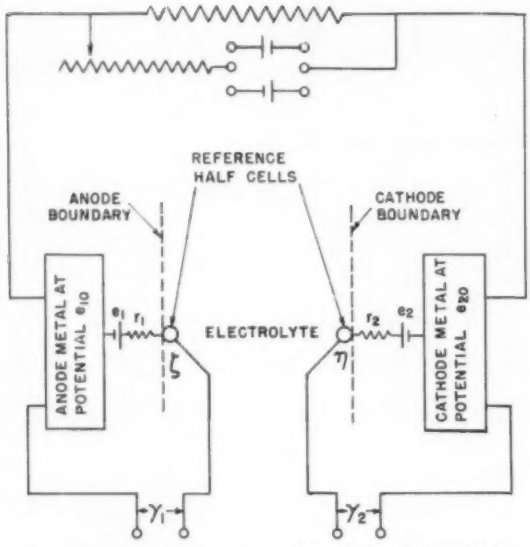

FIG. 3. Polarization of isolated anode and cathode

The argument is as follows. Under certain conditions single anodes and cathodes may be isolated that are large enough to study experimentally. In Fig. 3 an isolated anode and cathode in an electrolyte are represented schematically. An electric circuit is so arranged that an arbitrary external current may be imposed in either direction between the anode and cathode. Close to each electrode surface (ideally on the electrode boundary) so as to avoid ohmic drops in the solution is placed a salt bridge to a reference half-cell with half-cell potential Θ. The potential difference between the anode metal and the lead wire to the half cell is γ_1 ; between the lead wire and the cathode metal, γ_2 . The salt bridge on the anode boundary is located at the point ζ and the one on the cathode boundary is at η. $V(\zeta)$ and $V(\eta)$ are the potentials at ζ and η, respectively. The current flowing in the solution between the electrode boundaries is i and is positive if the direction of flow is from anode to cathode, and negative otherwise. The "half-cell potential" of the anode is P_1 and that of the cathode P_2 ; the potential in the metal phase at the anode is e_{10} and at the cathode e_{20} . By definition

$$P_1 = V(\zeta) - e_{10} \qquad [29]$$

$$P_2 = V(\eta) - e_{20} \qquad [30]$$

Consider first the anode polarization in terms of the notation of Fig. 3. Kirchoff's law requires:

$$V(\zeta) = e_{10} + e_1 - ir_1$$

When $V(\zeta) - e_{10}$ has been eliminated between this and [29] and the resulting equation differentiated with respect to i there results:

$$\frac{dP_1}{di} = \frac{de_1}{di} - i\frac{dr_1}{di} - r_1 \qquad [31]$$

Since r_1 is always nonnegative, in the simple case when e_1 and r_1 are constants:

$$\frac{dP_1}{di} = -r_1 < 0 \qquad [32]$$

That is, the anode polarization curve is strictly decreasing. As a matter of fact it is one of the fundamental assumptions of corrosion theory that regardless of whether e_1 and r_1 are constant or not, the anode polarization curve is monotonic decreasing; although in general it is not linear as in the simple case described by equation [34]. Furthermore the assumption is usually made (and is made here) that the polarization curves of microscopic anodes, as well as of anodes large enough to be isolated, are monotone decreasing. Monotonicity implies

$$\frac{dP_1}{di} \leq 0$$

Therefore equation [31] implies

$$\frac{de_1}{di} - i\frac{dr_1}{di} - r_1 \leq 0 \qquad [33]$$

Consider next the cathode polarization:

$$V(\eta) = e_{20} + e_2 + ir_2$$

Elimination of $V(\eta) - e_{20}$ between this equation and [30], and differentiation with respect to i yields,

$$\frac{dP_2}{di} = \frac{de_2}{di} + i\frac{dr_2}{di} + r_2 \qquad [34]$$

When e_2 and r_2 are constants

$$\frac{dP_2}{di} = r_2 \geq 0$$

Then by analogy with the anode case the proper assumption is that the cathode polarization curve is monotone increasing, regardless of whether e_2 and r_2 are constants. Therefore,

$$\frac{de_2}{di} + i\frac{dr_2}{di} + r_2 \geq 0 \qquad [35]$$

The sign conventions here are consistent with those adopted earlier in connection with the Müller-Cupr model of corrosion. Therefore in that model postulates [33] and [35] become,

$$\frac{\partial E_{1j}}{\partial I_{1j}} - I_{1j}\frac{\partial R_{1j}}{\partial I_{1j}} - R_{1j} \leq 0 \qquad [36]$$

$$\frac{\partial E_{2j}}{\partial I_{2j}} + I_{2j}\frac{\partial R_{2j}}{\partial I_{2j}} + R_{2j} \geq 0 \qquad [37]$$

These inequalities apply for each j. The subscripts 1 and 2 appear here with I because unlike the case when the anode and cathode may be separated,

$$I_{1j} \gtrless I_{2j}$$

In view of equation [13], [37] may be rewritten $\mu_j \geq 0$. On multiplication of equation [36] by -1 and reversal of its sense there results

$$\lambda_j \geq 0$$

Thus the inequalities [28] have been verified. An immediate consequence of [28] and [13] is

$$0 \leq \Delta_j \leq 1 \qquad [38]$$

except in the singular case when λ_j and μ_j both vanish, which need not be considered here.

Differentiation of equation [1] with respect to x and substitution of [27] in the equation for the derivative yields,

$$\frac{\partial I_1}{\partial x} = \left(\frac{1}{\frac{\partial \Gamma}{\partial I_3} + W}\right)\left[-\frac{\partial \Gamma}{\partial x}\sum_{j=1}^{N}\Delta_j H_j - I_3\frac{\partial \Gamma}{\partial x}\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3} + I_3\left(\frac{\partial \Gamma}{\partial I_3} + W\right)\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial x}\right. \qquad [39]$$
$$\left. - \sum_{j=1}^{N}\Delta_j\psi_j H_j - I_3\sum_{j=1}^{N}\Delta_j\psi_j\frac{\partial H_j}{\partial I_3}\right]$$

In order to obtain an important result in as simple a manner as possible the local cells are assumed identical, as a special case. Then the same result will be proved in a more general case by means of a statistical argument. If all the cells are identical, the Δ_j are all equal to some Δ and the ψ_j to some ψ. Then:

$$\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3} = \Delta\sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3}$$

$$\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial x} = \Delta\sum_{j=1}^{N}\frac{\partial H_j}{\partial x}$$

$$\sum_{j=1}^{N}\Delta_j\psi_j\frac{\partial H_j}{\partial I_3} = \Delta\psi\sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3}$$

But [21] implies

$$\sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3} = \sum_{j=1}^{N}\frac{\partial H_j}{\partial x} = 0$$

Therefore [39] reduces to

$$\frac{\partial I_1}{\partial x} = \frac{\left(-\frac{\partial \Gamma}{\partial x}\sum_{j=1}^{N}\Delta_j H_j - \sum_{j=1}^{N}\Delta_j\psi_j H_j\right)}{\frac{\partial \Gamma}{\partial I_3} + W} \qquad [40]$$

To remove the restriction that the local cells be identical in the derivation of [40] consider the terms in [39] containing the expressions

$$\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3}; \quad \sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial x}; \quad \text{and} \quad \sum_{j=1}^{N}\Delta_j\psi_j\frac{\partial H_j}{\partial I_3} \qquad [41]$$

Equations [13] and [19] imply that the Δ_j and ψ_j are partly but not entirely independent of the $\partial H_j/\partial x$ and $\partial H_j/\partial I_3$. However, the partial functional relationships linking these two sets of quantities are extremely complicated in nature, being unknown solutions of a set of differential equations. In order to reduce the problem to manageable proportions it is necessary to invoke a statistical assumption, i.e., that the complicated partial relationships associate the Δ_j and ψ_j with the $\partial H_j/\partial I_3$ and $\partial H_j/\partial x$ in a random manner. More specifically, the Δ_j and ψ_j are distributed in some way about their respective means. It will be assumed that these distributions are independent of the distributions of the $\partial H_j/\partial I_3$ and $\partial H_j/\partial x$ for every value of I_3 and x. It should be noted that this assumption is somewhat more plausible when the corroding surface is macroscopically homogeneous than when unevenly pitted.

Define G to be the statistical expected-value function. If f is the distribution function of the Δ_j define

$$M = G(\Delta_j) = \int_{-\infty}^{\infty}\Delta_j f(\Delta_j)\,d\Delta_j$$

In view of the constancy of the $\frac{\partial H_j}{\partial I_3}$ and $\frac{\partial H_j}{\partial x}$ for fixed I_3 and x, and the assumed independence of the Δ_j,

$$G\left(\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3}\right) = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3}\prod_{k=1}^{N}f(\Delta_k)\,d\Delta_k$$
$$= \sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\Delta_j\prod_{k=1}^{N}f(\Delta_k)\,d\Delta_k$$
$$= \sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3}\int_{-\infty}^{\infty}\Delta_j f(\Delta_j)\,d\Delta_j$$
$$= \sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3}G(\Delta_j) = M\sum_{j=1}^{N}\frac{\partial H_j}{\partial I_3} = 0$$

Similarly,

$$G\left(\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial x}\right) = 0$$

and

$$G\left(\sum_{j=1}^{N}\Delta_j\psi_j\frac{\partial H_j}{\partial I_3}\right) = 0$$

On replacing the expressions, [41] by their expected values (i.e., by zero) in [39], that equation is reduced to [40] in the general case.

Since the absolute value of a sum never exceeds the corresponding sum of absolute values equations [20], [38], and [40] imply

$$\left|\frac{\partial I_1}{\partial x}\right| \leq \frac{\left|\frac{\partial \Gamma}{\partial x}\right| + \left|\sum_{j=1}^{N}\psi_j H_j\right|}{\left|\frac{\partial \Gamma}{\partial I_3} + W\right|} \qquad [42]$$

The inequality [42] provides a measure of the ability of a chemical agent to inhibit corrosion by polarizing local cathodes, but yields no direct information regarding anodic inhibition. To see why this is so consider the case of a strictly cathodic additive, i.e., a chemical agent that may alter the polarization of local cathodes, but which has no effect on local anodes. If such an agent is present in solution at concentration, x, then the R_{2j} and E_{2j} are the functions of x and I_{2j} defined by [4]. However, R_{1j} and E_{1j} are independent of x by hypothesis, although they are functions of the current densities at the local anodes. That is,

$$E_{1j} = R_{1j}(I_{1j})$$

$$R_{1j} = R_{1j}(I_{1j})$$

Hence [13] implies that $\psi_j = 0$ for every j. Therefore, in the case of a strictly cathodic inhibitor, [42] simplifies to

$$\left|\frac{\partial I_1}{\partial x}\right| \leq \frac{\left|\frac{\partial \Gamma}{\partial x}\right|}{\left|\frac{\partial \Gamma}{\partial I_3} + W\right|} \qquad [43]$$

Note that the left-hand member of equation [43] is a measure of the effectiveness of the inhibitor under investigation. If $\partial I_1/\partial x$ can be determined at several concentrations of the inhibitor ranging from zero to x_o, the maximum concentration of interest, and at zero external current, the area under the graph of $\partial I_1/\partial x$ vs. x from 0 to x_o is

$$\int_o^{x_o} \frac{\partial I_1}{\partial x}\, dx = I_1(x_o) - I_1(o) \qquad [44]$$

This is just the decrease in corrosion current brought about by increasing the inhibitor concentration from 0 to x_o, which is proportional by Faraday's law to the change in corrosion rate effected by the inhibitor. Thus, if $\partial I_1/\partial x$ is negative and large in absolute magnitude on the interval $0 - x_o$, the inhibitor is a good one. Otherwise it is not.

Observe next that the three quantities in the right-hand member of inequality [43] may be measured experimentally. If the inhibitor concentration is fixed and observations of Γ are made at several values of I_3, the slope of the graph of Γ vs. I_3 at any value of I_3 is $\partial\Gamma/\partial I_3$ at that value. Of course, the value of I_3 of greatest interest is zero since it is usually desired to determine the effectiveness of inhibitors in the absence of any external current. Similarly $\frac{\partial \Gamma}{\partial x}$ may be measured at $I_3 = 0$. In some instances W may be computed from [3] by taking z to be the distance from the reference half-cell to the metal surface. If this estimate of z is not good enough, W may be determined by one of the methods suggested by Pearson (4). Or measurements of $\partial\Gamma/\partial x$ and $\partial\Gamma/\partial I_3$ with two half-cells at different distances from the metal surface may be substituted in equation [40] with the ψ_j all zero since $\partial I_1/\partial x$, and $\sum_{j=1}^{N} \Delta_j H_j$ are independent of the location of the reference half-cell. Specifically, if W_1 and W_2 are the values of W for two different positions of the reference half-cell, $(W_2 - W_1)$ can be measured easily. Then

$$W_1 = \frac{\left(\frac{\partial\Gamma}{\partial x}\right)_1\left(\frac{\partial\Gamma}{\partial I_3}\right)_2 - \left(\frac{\partial\Gamma}{\partial x}\right)_2\left(\frac{\partial\Gamma}{\partial I_3}\right)_1 + \left(\frac{\partial\Gamma}{\partial x}\right)_1 (W_2 - W_1)}{\left(\frac{\partial\Gamma}{\partial x}\right)_2 - \left(\frac{\partial\Gamma}{\partial x}\right)_1} \qquad [45]$$

Since all of the terms in the right-hand member of this equation can be measured, W_1 may be computed.

Conclusions

The right-hand member of [43] determines an upper bound for $|\partial I_1/\partial x|$ whose value can be found experimentally. If the upper bound is small over the entire concentration range of interest, then $|\partial I_1/\partial x|$ is small over the same range and [44] implies that the inhibitor is not very effective. On the other hand, if the upper bound is large, no conclusion can be drawn. The inhibitor may be a good one or it may not. Some other technique must be used to decide ultimately whether agents for which $\left|\frac{\partial\Gamma}{\partial x}\right| \Big/ \left|\frac{\partial\Gamma}{\partial I_3} + W\right|$ is large are good inhibitors. What the method described here does provide is a rapid screening method that eliminates from further consideration materials that certainly are not good cathodic inhibitors.

In the general case when the chemical agent is not a strictly cathodic inhibitor equation [42] implies that [43] may be in error by as much as Q, where

$$Q = \left|\frac{\sum_{j=1}^{N} \Delta_j \psi_j H_j}{\frac{\partial\Gamma}{\partial I_3} + W}\right|$$

Unfortunately, Q cannot be measured directly. Note, however, that its value, for all practical purposes, depends only on the effectiveness of the chemical

agent in polarizing (or depolarizing) the local anodes. Hence equation [43] remains valid provided $\partial I_1/\partial x$ is interpreted as the component of the derivative of the corrosion current with respect to concentration that results from the polarization or depolarization of the local cathodes by the agent. That is, equation [43] provides a method for screening chemical agents as cathodic inhibitors regardless of whether the agents also function as anode polarizers or depolarizers. The inequality, however, provides no information regarding anode polarization. In principle, it is possible to calculate Q as well as $\partial I_1/\partial x$ and $\sum_{j=1}^{N} \Delta_j H_j$ from four measurements of $\partial\Gamma/\partial x$ and $\partial\Gamma/\partial I_3$ by the same procedure that was used to derive equation [45]. It is very unlikely, however, that the method would be feasible experimentally. Although the author intends soon to undertake an experimental verification of [43] no measurements have yet been made. Experiments should shed light on the question of whether the electrochemical theory of corrosion can be applied quantitatively to inhibitor studies.

It is interesting to note that, if the agent added to the system under investigation is a cathode polarizer, equation [43] may be written,

$$0 < -\frac{\partial I_1}{\partial x} \leq \frac{\partial\Gamma/\partial x}{\dfrac{\partial\Gamma}{\partial I_3} + W} \qquad [46]$$

Equation [26] implies

$$\frac{\partial\Gamma}{\partial I_3}\sum_{j=1}^{N}\frac{1}{\lambda_j} = -\sum_{j=1}^{N}\Delta_j H_j - I_3\sum_{j=1}^{N}\Delta_j\frac{\partial H_j}{\partial I_3} - W\sum_{j=1}^{N}\frac{1}{\lambda_j}$$

Or since the statistical expectation of the second term on the right is zero

$$\frac{\partial\Gamma}{\partial I_3} = \frac{-\sum_{j=1}^{N}\Delta_j H_j}{\sum_{j=1}^{N}\dfrac{1}{\lambda_j}} - W$$

In the first term on the right of this last equation Δ_j, H_j, and λ_j are positive for every j. Therefore, the first term is negative. Since W is positive the second term is also negative, which implies that is negative. Therefore

$$\left|\frac{\partial\Gamma}{\partial I_3}\right| = -\frac{\partial\Gamma}{\partial I_3}$$

It can be shown similarly that

$$\left|\frac{\partial\Gamma}{\partial I_3} + W\right| = -\frac{\partial\Gamma}{\partial I_3} - W$$

and that for cathode polarizers

$$\left|\frac{\partial\Gamma}{\partial x}\right| = -\frac{\partial\Gamma}{\partial x}$$

Substitution of these values in [43] yields [46].

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

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